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qualitative analysis



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Fundamentals of
SEMI-MICRO QUALITATIVE ANALYSIS

BY CARL J. ENGELDER

FUNDAMENTALS OF SEMI-MICRO
QUALITATIVE ANALYSIS

Cloth; 6 by 9½; 389 pages.

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Fundamentals of
SEMI-MICRO
QUALITATIVE ANALYSIS

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PREFACE

The normal text book of qualitative analysis follows the somewhat standard pattern: a lengthy section on equilibrium theory, the properties and analytical reactions of the cations and their separation and detection, a similar treatment for the anions, and a closing section on systematic analysis. The instruction in theory must, perforce, be spread over the duration of the course, whereas, in following the conventional order, the laboratory work plunges the student prematurely into all the complexities of cation groups I and II, long before he, on the one hand, has acquired necessary experimental experience and technique and, on the other hand, has gained a sufficient understanding of the underlying theory. To overcome these difficulties, a rearrangement of the course of instruction is presented in this book, based upon the author's successful experience over the past five years.

The course of instruction begins with the alkali metals and proceeds into a study of the alkaline earth elements, during which time the solubility product principle is introduced. This is followed by the laboratory study of the metals of cation group III, offering thus an appropriate introduction to oxidation theory with iron, manganese, and chromium as examples; amphotericism as illustrated by aluminum, chromium, and zinc; and the theory of complex ions as exhibited by nickel, cobalt, and zinc. By the time this phase of instruction is completed, the student is better conditioned both in theory and practice to understand and carry out the more difficult reactions, steps and procedures of groups I and II. Common-ion effect or buffering is incorporated here in the theory. Arsenic forms the transition from cation analysis to anion analysis. Remaining sections of theory are included in the chapters on anion study. For complete systematic analysis, anion procedures precede cation procedures.

The most important features of this book are (1) the introduction of the cations, in reverse order, before complete systematic analysis is undertaken and (2) the gradual introduction of selected portions of theory at appropriate intervals to accompany the ex-

perimental work. The author believes he has successfully integrated theory with practice. A schedule of laboratory and classroom assignments is suggested in the appendix to aid the teacher in planning his course based on this new arrangement.

Incorporated in the sections on theory are numerous illustrative calculations followed by problem sets, ten in all, each set comprising 20 problems, half with and half without answers. This provides ample material for instruction in chemical calculations, thus dispensing with the use of a separate problem book.

Portions of this book have been taken from the first and second editions of *Semi-Micro Qualitative Analysis* by Engelder, Dunkelberger, and Schiller.

CARL J. ENGELDER

PITTSBURGH, PA.

June 1946

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PART I. THE CATIONS

CHAPTER I

INTRODUCTION. REACTIONS AND EQUATIONS. APPARATUS AND TECHNIQUE. REAGENTS

Analytical chemistry deals with the methods and principles involved in determining the composition of matter. A qualitative analysis reveals what constituents are contained in a given material, and a quantitative analysis determines how much of each is present. Various chemical and physical methods and instruments are employed in the examination, utilizing the differences in the chemical and physical properties of the constituents as a means of identifying the constituents and determining the amount of each present. In qualitative chemical analysis the identification depends for the most part upon the chemical properties of the constituent; the methods therefore involve, in general, a separation of the constituents one from another by applying suitable chemical reactions, followed by the addition of appropriate reagents which give distinctive identifying tests. In the broadest sense qualitative analysis includes the identification of any substance—animal, vegetable or mineral—present either by itself or mixed with other substances.

Elementary qualitative analysis, moreover, deals almost exclusively with mixtures of relatively simple inorganic compounds. The only organic compounds considered are salts of several organic acids. In the qualitative analysis of such a mixture the procedure for the separation and identification of the metal constituents (cations) is carried out on one portion of the sample, whereas the acid radicals (anions) are detected by applying another scheme of separation and identification to another portion of the sample. It is therefore impossible to state what particular compounds are present in a mixture of compounds. To illustrate, if a sample, consisting of K_2SO_4 , $NaNO_3$ and $CuCl_2$, is dissolved and analyzed, the analyst would detect in the cation analysis the presence of

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potassium, sodium and copper, and in the anion analysis the presence of sulfate, nitrate and chloride ions; analysis of a mixture of KNO_3 , NaCl and CuSO_4 however would lead to exactly the same result. Moreover, only a limited number of metal ions and of acid radicals is considered in elementary qualitative analysis.

Methods of qualitative analysis were devised early in the development of chemistry. These methods have undergone and are still undergoing modifications, as better methods of separation are devised and as newer and more sensitive tests are developed. As far as the scale of operations or the total amount of material handled is concerned, there are today three more or less distinct techniques. The first and oldest of these is the macro technique in which beakers, flasks, funnels and test tubes of the usual size are employed and where the volumes of solutions are relatively large, ranging from several milliliters up to 100 ml. or more. At the other extreme is the truly micro technique, with its highly specialized, diminutive apparatus; the microscope is employed as an important adjunct, and the volumes of test materials usually are not more than several cubic millimeters. Intermediate between these two is the special technique or mode of operation upon which the procedures in this book are based (the author has termed this technique "semi-micro"); it has borrowed methods and appliances from the other two techniques. It is partly macro and partly micro chemical.

Among the features which characterize and define this technique are: (1) the volumes of solutions and amounts of material are limited so that group precipitations, separations, washings and similar operations generally are confined to 1 or 2 ml. of solution; (2) identifying tests are made with drop portions of test substance and reagents, the reacting solutions being brought together in small test tubes or centrifuge tubes, on spot plates, glass slides or drop-reaction paper; and (3) "filtrations" are conducted ordinarily by centrifugation. The microscope is not employed in the methods described here.

There are no sharp boundaries among these three techniques, and obviously there is some overlapping. The technique is necessarily determined by the amount of material handled; this in turn depends upon the size of the sample, the weight of each constituent in the sample and the volume of the solution. The whole matter is governed, in practice, by the conditions which it is possible to establish in order to obtain a fairly sensitive positive test for the

presence of any given constituent. By the term "sensitivity" is meant the quantity of material which responds to the test reagent; if the quantity of test ion refers to its concentration, that is, the amount present in a given volume, the limit of sensitivity is reached when a more dilute solution fails to give the test. If the absolute quantity of test substance, usually expressed in weight, is referred to, the sensitivity of a reaction is expressed in terms of actual weight of the test ion. The unit of microchemical weight is 1 microgram ($1 \mu\text{g.}$) or 1 gamma (1γ), that is, 0.001 milligram, or 0.000001 gram. Accordingly, on this definition of sensitivity, the limit of identification ranges from 1 milligram to much less than 0.1 microgram, depending on the technique employed. The sensitivity of a test depends, too, on the amounts of other substances present in the mixture when the test reagent is applied, for which the term "limiting proportions" is used.

In the field of qualitative analysis, during the past two decades, an enormous amount of work has been done, the object of which has been to find extremely sensitive reagents and specific reactions which would give tests for certain ions in the presence of other ions. The current chemical literature contains a wealth of published information on the results of such investigations. To Fritz Feigl in particular much credit is due for his contribution, *Qualitative Analyse mit Hilfe von Tüpfel reaktionen*,¹ which is the authoritative reference. Feigl gives an excellent discussion of a considerable number of specific and highly sensitive reactions conducted as spot and drop tests, less attention being given to systematic separations.

Learning the procedures and acquiring the skills necessary to separate and identify the constituents of a mixture is, of course, a primary aim in any course in qualitative analysis. But to an ever-increasing extent the course of instruction in qualitative analysis is being recognized as the most favorable place to present and review, to emphasize and apply many of the fundamental principles upon which not only it but also all of chemistry is based. This is as it should be, for it is only by the understanding, appreciation and application of such fundamental information that really intelligent progress can be made in scientific work.

Students frequently are concerned about the relative emphases placed upon the "theoretical" and the "practical" in their courses.

¹ Available in English translation from the third German edition, Norde-mann Publishing Co., New York, 1939.

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Unfortunately, the word "theory" frequently seems to connote something indefinite and uncertain, probably incorrect or at least inaccurate, and of no conceivable usefulness or importance: in short, an unnecessary burden imposed upon students by an unsympathetic instructor. "Practical," on the other hand, seems to imply something of real importance, something directly applicable to everyday life. Such a distinction is absurd. If we interpret "theoretical" broadly, as we should, to mean the explanatory discussion which makes it possible not only to correlate the results of actual experiments but also to predict or calculate the results of untried experiments, we can say with conviction that nothing is so practical as a good theory and few things are so inefficient as practical work unguided by theoretical information.

The fundamental laws of chemical change which underlie and control all chemical reactions are so amply illustrated and so frequently encountered in the laboratory work of qualitative analysis that the student should acquire a thorough grasp and understanding of the basic principles of chemistry. The two fundamental laws are (1) the Law of Definite Proportions (closely related to the Law of Combining Weights) and (2) the Law of Chemical Equilibrium. The former states that the weights of reacting components are proportional to the atomic or molecular weights of the elements concerned; its application enables one to calculate the proportions in which elements are united in compounds as well as to determine how much product is formed, or how much reagent is required in a (practically complete) chemical reaction. The Law of Chemical Equilibrium, on the other hand, controls in part the extent of a reaction and enables one to calculate the concentrations of reactants and products which are present when equilibrium is reached.

To comprehend fully and apply competently both laws to chemical reactions requires more time than reasonably can be allotted to the study of qualitative analysis alone. It has been customary therefore to direct the study, in the course of instruction of qualitative analysis, to the applications of the Law of Chemical Equilibrium and to reserve a more intensive study and application of direct proportion and combining weights for the course in quantitative analysis. Equilibrium theory therefore is emphasized in qualitative analysis; the student however should realize that reaction by direct proportion is nonetheless operative here and, further, that the equilibria attained in reactions that are carried

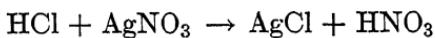
out quantitatively are even more important than when applied to the same reaction encountered in the qualitative procedures.

The study of chemical equilibria and their applications to the several different types of reactions constitutes the most important part of the theory of qualitative analysis. A theory or fundamental law can only be adequately understood and appreciated when it is reduced to a rigorous mathematical test—hence the numerous problems which accompany the sections on theory throughout this book. The student should not regard the weekly problem assignments as mere exercises in algebra; on the contrary, the correct solution of a problem is proof to him that he comprehends and can apply a certain principle. A fair knowledge of algebra and a working facility with exponents and logarithms are essential. A brief review of mathematical operations is given in the Appendix.

REACTIONS AND EQUATIONS

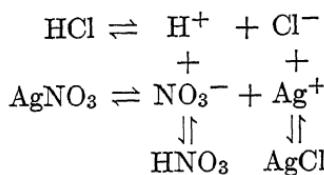
The study of the reactions encountered in the procedures of qualitative analysis constitutes one of the most important parts of the student's work, since, naturally, the methods of separation and identification are based on suitably selected reactions. Reactions, to be of the greatest service in bringing about sharp separations and distinctive tests, must run practically to completion. In aqueous solutions most reactions are ionic and attain equilibria quickly.

Ionic Nature of Reactions. Since most of the reactions of qualitative analysis take place in aqueous solutions of ionized electrolytes, the actual chemical changes involved must be considered as taking place between ions and not between the non-ionized components of the solute. In other words, we are concerned almost entirely with ionic reactions, and the reactions therefore are represented as ionic and not molecular equations. An example will make this clear. Suppose we take a solution of AgNO_3 and add to it dilute HCl . A curdy white precipitate of AgCl will form at once. The same result can be obtained by mixing a solution of NaCl , NH_4Cl , BaCl_2 or other soluble chloride with the solution of any soluble silver salt. If the reaction were expressed as a molecular equation thus,

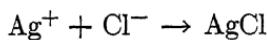


it would imply a reaction between molecules. But in aqueous solutions AgNO_3 , HCl and NaCl are dissociated into their respective

ions. The complete scheme by which reactions of this kind can be represented is



This double decomposition reaction indicates that Ag^+ ions and Cl^- ions are removed from the solution in the form of a slightly soluble precipitate of AgCl , leaving H^+ ions and NO_3^- ions, equivalent to the appearance of HNO_3 in the solution. It is not accurate to say that HNO_3 is formed in this reaction; it merely happens that the ions constituting it are left after the other ions are removed. The formula of silver chloride is underscored to indicate that AgCl is only slightly soluble and therefore forms a precipitate, causing the reaction to go practically to completion toward the right. Only the Ag^+ ions and Cl^- ions are concerned in the reaction; so, for simplicity, we express the change as a simple ionic equation:



The student early must acquire this ionic point of view and consider all reactions, with but few exceptions, as taking place between the ions concerned.

Classification of Ionic Reactions. In general, it can be stated that an ionic reaction takes place and in most cases runs practically to completion whenever *ionic concentrations are decreased*. The concentrations of the reacting ions can be diminished in one of two general ways, namely (1) by ions uniting and (2) by ions transferring one or more electrons. These are the two important classes of reactions. In the first class are included several types, the reaction taking place because:

- (a) A precipitate is formed, since in the formation of a solid ions are removed from solution.
- (b) A complex ion is formed.
- (c) A weakly ionized acid or base or, in rare cases, a weakly ionized salt is the product of the reaction. Neutralization reactions also come under this heading, since the fundamental reaction here is the union of H^+ and OH^- to form water; and closely allied to this are the reactions in which an amphoteric form is altered. Included here are also the reactions of hydrolysis. We should

remember, further, that certain weakly ionized substances are gases, and therefore their liberation aids in the removal of ions from solution.

Reactions of the second class, namely, those in which electrons are transferred from one ion to another and thereby diminish the ionic concentrations of the initial reactants, are the important and frequently encountered oxidation-reduction reactions. Such reactions hereafter will be spoken of as *redox reactions*, the word "redox" being derived from the term "reduction-oxidation." The other class of reactions accordingly will be referred to as *non-redox reactions*.

The equilibrium relationships based on this classification of ionic reactions constitute the most important part of the study of the fundamental principles of qualitative analysis. This is discussed in greater detail in Chapter III.

The Writing and Balancing of Chemical Equations. The writing of equations and the ability to balance them correctly must be acquired before any intelligent progress can be made in the study of analytical chemistry. A chemical equation cannot be written and balanced unless the reactants and products are known. What takes place in a reaction must be discovered by experiment. The equation must represent what actually takes place.

If the formulas of the compounds or ions involved are known, it is usually a comparatively simple matter to balance the coefficients. A great many equations can be balanced by inspection. Where the actions are more complicated, writing the equations in steps and canceling out the components that are common to the two successive reactions usually will result in a correctly balanced final equation. Special consideration is given in a later section, Chapter IV, to oxidation-reduction or *redox* equations, which usually are the most difficult to balance.

Inasmuch as most of the reactions with which we are concerned are between ions, the equations representing such reactions are written as ionic equations. In this book the simple ionic form usually will be used, which shows only those ions and products which are mainly involved in the reactions. Sometimes reactions will be given in molecular form, whenever such chemical changes can be more clearly comprehended and the chemical relationships better shown; it must be understood, however, that the reaction is always ionic, even though for certain purposes or emphasis the reaction may be expressed in molecular form. The equations for

ionic reactions which lead to the formation of precipitates, of less ionized products, of complex ions and of amphoteric changes usually are easy to balance, the selection of the correct coefficients being ordinarily a matter of simple inspection.

In writing equations of this kind, only the essential ions and molecules which take part in the reaction should be put into the equation. Highly ionized substances, such as strong acids, alkalies and salts, in general should be stripped of their non-essential ions, whereas weakly ionized substances may be written in the molecular form. Among the weakly ionized substances are included H_2S , $\text{HC}_2\text{H}_3\text{O}_2$, NH_4OH or NH_3 , and H_2O . Precipitates and gases, of course, are formulated as molecules.

Conventions Used in Writing Equations. The following rules are to be applied in the use of symbols or signs which appear in a chemical equation:

1. Whenever it is the purpose merely to indicate the direction or the tendency of the chemical change (sometimes even without an attempt to balance the equation) or to illustrate the methods of balancing the equation, a wavy arrow (\rightsquigarrow) is employed. See, for example, page 99.)
2. If a balanced equation for a practically complete reaction is expressed, the simple arrow (\rightarrow) is used.
3. When special attention is to be called to an equilibrium relationship, that is, to the reversibility of a reaction, the reversible sign (double arrows, \rightleftharpoons) is used.
4. A precipitate is indicated by underscoring the formula, and a gas or volatile compound by overscoring.
5. A small circle ($^\circ$) written above and to the right of the symbol indicates an element in the atomic, electrically neutral state.

THE APPARATUS AND TECHNIQUE OF SEMI-MICRO ANALYSIS

The apparatus used and the technique followed in the semi-micro methods of qualitative analysis described in this book are so simple that no lengthy description is deemed necessary. The apparatus listed in the Appendix has been found ample for the work at hand. Except for the centrifuge, one of which can be shared by several students, each student's outfit consists of such relatively simple items as centrifuge tubes, test tubes, a spot plate, drop-reaction paper, glass slides, medicine droppers, and reagent vials for an individual set of reagents.

Preparatory Laboratory Work. The preliminary assignments in the laboratory, before the actual experiments and study of the reactions are begun, consist of two general parts: (1) preparation of certain pieces of apparatus and equipment and (2) assembly of the necessary reagents.

In connection with the first, check over the contents of the locker assigned you, and report and replace missing or damaged apparatus. Procure the non-returnable apparatus if this has not been supplied. Seal the piece of platinum wire in a short length of glass tubing. Draw out a medicine dropper to a thin capillary tube by heating in a hot flame; this will be your capillary pipet. Follow the instructions given by the laboratory instructor for the making of a wash bottle and other pieces of apparatus required.

Certain general instructions regarding the assembling of the reagent kit and preparation of a few reagents are given in the section on assembling of reagents.

Semi-Micro Technique. The technique employed in carrying out the methods described in this book is simple and so easily acquired that no special provision in the form of preliminary experimentation is made. The more important operations and manipulations are described in the following.

Precipitation. Precipitations are carried out by the following methods:

1. In a centrifuge tube. The precipitating agent is added to the solution in a centrifuge tube. The advantage of this procedure lies in the ease with which the precipitate may be observed after centrifuging and the facility with which a separation can be carried out.

2. On the spot plate. Here a drop of the solution to be tested is brought into contact with a drop of the precipitating agent in the cavity of a spot plate. This procedure is effective for detecting the formation of colored precipitates. Black spot plates sometimes are used for observing white precipitates.

3. On a glass slide. In this method a drop of the solution and one of the precipitant are placed side by side on a slide, and then the two are mixed by means of a stirring rod or a platinum wire. When heating is necessary, the drops are placed as near to one corner of the slide as possible and the heat from a burner cautiously applied.

Filtration. Since most of the precipitations in the semi-micro procedures are carried out in centrifuge tubes, the main filtration

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operations are concerned with removing the supernatant liquids (centrifugate) from the precipitates. This is best accomplished by using a medicine dropper or capillary pipet. The bulb of the pipet first is compressed to expel all the air and then is carefully introduced into the centrifuge tube containing the liquid and precipitate. The tip of the pipet should be brought as close as possible to the precipitate, and then the bulb is gently released. If the operation is conducted successfully, the liquid drawn into the pipet should be clear and the precipitate undisturbed. In some cases where it is difficult to do this, a small plug of cotton may be placed in the tip of the pipet. This will filter out any particles of the precipitate.

If washing of the precipitate is required, a few drops of wash solution are added, the precipitate stirred with a platinum wire or thin glass rod, the mixture centrifuged and the centrifugate drawn off with a medicine dropper.

Color Reactions. These are carried out on drop-reaction paper. Such methods usually are more sensitive than those carried out on a spot plate or glass slide, owing to the concentration of the solution in the capillary pores of the paper.

With certain of these reactions, the colors are brought out or "developed" by allowing hydrochloric acid vapor or ammonia fumes to come into contact with the reaction mixture on the paper. This is done by holding the reaction paper in the fumes evolved either by heating a few drops of concentrated HCl or NH₄OH, as the case requires, in a crucible, or else by passing the paper over the mouth of the reagent bottle containing the concentrated acid or ammonia.

Evaporation. Evaporations are carried out by transferring the solution to a crucible and carefully heating. The heating may be conducted by placing the crucible in a water bath; this procedure lessens the danger of solution losses due to spattering. When the crucible is heated directly, care must be exercised to prevent super-heating, in which case solution will be lost. The container should be kept moving continually while being heated.

Cleanliness. Absolute cleanliness is essential to successful use of semi-micro methods. All apparatus should be cleaned thoroughly with cleaning solution and then rinsed several times with distilled water. All pipets and stirring rods should be kept in a beaker of distilled water and should be rinsed before using. Immediately after any equipment has been used, it should be rinsed and then placed

in cleaning solution; the pipets should be rinsed several times with distilled water and then placed in a beaker containing distilled water.

Soap solution or sodium phosphate frequently are employed as the cleaning substance. Dichromate cleaning solution may be used in place of either of the other two. In order that this cleaner be sufficiently cool before the close of the laboratory period, it is imperative that its preparation be attended to immediately.

The dichromate cleaner is made as follows: Dissolve 50 grams of commercial $\text{Na}_2\text{Cr}_2\text{O}_7$ in 150 ml. of warm water. Cool and add slowly, with constant stirring, 230 ml. of commercial H_2SO_4 . The mixing is best done in a large evaporating dish. When it is thoroughly cool, at the close of the laboratory period, transfer to a 500-ml. wide-mouthed bottle and use as required. This cleaning mixture can be used repeatedly as long as it remains red and thick.

Always rinse apparatus with distilled water immediately before use. Use distilled water sparingly.

Assembling of the Reagents. In the locker of your desk will be found a reagent rack and a considerable number of small (30-ml.) bottles and screw-cap vials (3-ml.) provided with dropping tubes, as well as small biological vials with corks. These are to contain your individual set of reagents. If these containers are not already labeled, labels will have to be prepared neatly and attached to the proper-sized bottle or vial.

In general, the 30-ml. bottles are to contain the reagents used in larger quantities such as the common acids and alkalies and the group precipitating reagents. These are as follows:

conc. HCl	dil. HCl
conc. HNO_3	dil. HNO_3
conc. H_2SO_4	dil. H_2SO_4
conc. NH_4OH	dil. NH_4OH
4 M KOH	4 M NaOH
$(\text{NH}_4)_2\text{CO}_3$	dil. $\text{HC}_2\text{H}_3\text{O}_2$
$\text{Ca}(\text{NO}_3)_2$	$\text{Ba}(\text{NO}_3)_2$
$\text{Zn}(\text{NO}_3)_2$	AgNO_3

Fill these bottles with the reagents designated from the stock supply except those for the dilute HCl, HNO_3 , H_2SO_4 and NH_4OH . These four dilute reagents are to be prepared from the concentrated ones by dilution as follows:

Place 10 ml. of concentrated HCl in the "dilute HCl" bottle and add 20 ml. of distilled water, making approximately 30 ml. of the diluted reagent. This is a 1:2 solution.

Likewise, for the dilute HNO_3 , dilute 10 ml. with about 20 ml. of water. This, too, is a 1:2 reagent.

In preparing the dilute H_2SO_4 , place 25 ml. of distilled water in the 30-ml. bottle and slowly add 5 ml. of concentrated H_2SO_4 . This is a 1:5 solution.

The dilute NH_4OH is made by mixing 15 ml. of concentrated ammonia reagent with 15 ml. of distilled water (a 1:1 dilution).

The large number of liquid reagents listed in the appendix are used in smaller quantities and some only infrequently. A number of them are supplementary or used only in optional tests. Some are unstable and will be supplied as needed. Still others will be dispensed by the instructor or placed at the disposal of the student at convenient locations in the laboratory. The instructor will furnish a list of those which are to be supplied for the student's individual set. These are to be supplied from the stock bottles and placed in the screw-cap vials, and labels are to be provided.

Solid reagents, from a list provided by the instructor, are to be placed in the corked vials.

Reagents Used in the Procedures of Analysis. Examination of the reagent list in the Appendix indicates that both solid and liquid reagents are included. The reasons for supplying some of the reagents in solid form are that (1) certain of these substances are insoluble, (2) some give unstable solutions and are prepared when a fresh solution is called for, and (3) more intensified reactions are obtained in certain cases when the reagent is added in the solid form rather than as a solution. With regard to the liquid reagents, the following observations might profitably be made, thereby providing a broad perspective of their general nature and method of preparation. Note that:

1. Some of the reagents are pure organic liquids such as ether, alcohols, chloroform, whereas the majority are solutions.
2. Water is the usual solvent, although organic liquids are used in the preparation of a few reagents.
3. Inorganic as well as organic compounds constitute the solutes.
4. Most of the reagents have been prepared by dissolving the specified amount of the solute in 100 ml. of the solvent. These are called "empirical" solutions.
5. The "concentrated" acids, namely, HCl , H_2SO_4 and HNO_3 , as well as NH_4OH , are designated by their specific gravity and percentage by weight. These designations are discussed further in the following section.

6. The reagent list indicates the purpose of the reagent when it is used as a final test reagent; when not so designated the reagents find their proper use throughout the procedures of analysis.

A general discussion of reagents including the various methods of designating their strength together with calculations based on their preparation and use follows.

REAGENTS

In the laboratory work of qualitative analysis, the experimenter is engaged primarily and continuously in observing the effect of reagents on test substances of known and unknown composition. In fact, from the experimental side it may be said that experimental qualitative analysis consists very largely in the intelligent selection and proper use of reagents. At the outset, therefore, in the study of this subject, the student must become acquainted with the reagents to be employed and learn how to carry out the calculations involved in the preparation and use of a wide variety of reagents.

In general, reagents are added to the test substances for the following purposes:

1. As precipitating reagents.
2. As solvents for dissolving precipitates, residues and samples.
3. For acidifying, neutralizing or rendering a solution alkaline.
4. As oxidizing or reducing agents.

There are several methods or systems in common use for preparing and for designating the strength of reagent and other solutions. Three of these systems bear a close relationship to the molecular weight of the solute; they are the (1) molar, (2) molal and (3) normal systems.

1. Molar Solutions. A molar solution contains the molecular weight in grams of the solute in a liter of solution. This system is of extreme fundamental importance in the theory of qualitative analysis. Although only a few of the laboratory reagents are actually designated in terms of their molarity, the units of mass or concentration used in this system, namely, the gram mole and gram ion, form the basis of the mathematical treatment of all equilibrium relationships. Molar concentrations are introduced in the following chapter and are used subsequently in practically all calculations throughout this book.

2. Molal Solutions. A molal solution contains one gram-molecular weight of the solute in 1000 grams of the solvent. Molal

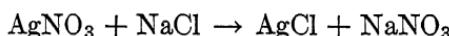
solutions are used extensively by the physical chemist. An example of a molal solution is found on page 24 where the boiling and freezing points of solutions are discussed.

3. Normal Solutions. This system of concentration, extensively employed in quantitative analysis, is sometimes used in qualitative analysis to indicate the strength of reagent solutions. A normal solution contains one gram equivalent weight of the solute per liter of solution. A gram equivalent weight is that amount of reactant which will bring into reaction, directly or indirectly, one gram-atomic weight (1.008 grams) of hydrogen. A normal solution of any acid therefore contains 1.008 grams of replaceable hydrogen per liter; if the acid is monoprotic (that is, supplies one hydrogen ion per molecule), such as HCl, HNO₃ or HC₂H₃O₂, the molecular weight in grams will furnish the required gram equivalent weight of hydrogen. A normal solution of H₂SO₄ contains one-half the molecular weight of H₂SO₄ in grams per liter of solution. Corresponding definitions hold for normal solutions of alkalies, of precipitating agents and of oxidizing and reducing agents.

4. Empirical Solutions. The solutions resulting from the dissolving of solid samples, as well as a great many of the reagent solutions, usually are designated "empirical" solutions. Each individual solution is prepared of a strength best suited for its particular use. The strength of these solutions may be expressed in grams of solute per liter, per 100 ml., or per milliliter. If expressed in grams of solute per milliliter the term titer is sometimes applied to the strength of such solutions. Thus a solution containing, for example, 0.050 gram of PO₄⁼ ion is said to have a phosphate titer of 0.050.

Example 1. How many milliliters of AgNO₃ solution containing 25.0 grams of AgNO₃ per liter are required to precipitate 0.015 gram of NaCl as AgCl?

The equation is



From the relation,

$$\text{AgNO}_3 : \text{NaCl} = x : 0.015$$

it is found that 0.044 gram of AgNO₃ is required.

Since in 1000 ml. of the reagent there are 25 grams of AgNO₃, in 1 ml. there will be 25.0/1000 or 0.025 gram. Therefore 0.044/0.025 or 1.76 ml. of the reagent will be needed.

5. Test Solutions. These solutions are of such a strength that in the series of cation solutions, the metallic-ion content is kept uniform (10 milligrams per milliliter for the stock supply and 1 mg per ml. for the student's use); and in the series of anion solutions, the anion content for the stock supply contains 10 milligrams per milliliter of the respective anion and for student use 2 milligrams per milliliter. Lists of cation and anion stock test solutions are given in the Appendix.

A series of cation test solutions (1 milligram of cation per milliliter) and a series of anion test solutions (2 milligrams of anion per milliliter) will be placed on a special reagent rack in the laboratory where they will be available to the student. These solutions are employed as the source of the cations and anions in carrying out the laboratory work described under "Preliminary Experiments."

The advantage resulting from the use of test solutions of uniform known strength lies in the fact that the sensitiveness of the test can be studied with better results. Some judgment can be formed of the relative amounts of each component present in a mixture if the preliminary work is carried out with solutions of known and equal strength. In this way a qualitative analysis may become an approximately quantitative one. The student always should exercise judgment in distinguishing traces from considerable quantities of a constituent found in the course of an analysis.

The calculations involved in the preparation of these test solutions illustrate a simple application of the Law of Definite Proportions. The following example will make this clear.

Example 2. How much AgNO_3 should be weighed out, dissolved and the solution made up to 1 liter, in order that in the preparation of the test solution each milliliter should contain 10 milligrams of Ag^+ ion (if it is assumed that all the silver is in the ionic condition)?

Since 1 ml. is to contain 10 milligrams or 0.01 gram, 1 liter (1000 ml.) will contain 1000×0.01 or 10 grams of Ag^+ ion. It is then a simple matter to calculate the weight of AgNO_3 required to furnish 10 grams of silver.

Since

$$\text{Ag : } \text{AgNO}_3 = 10 \text{ grams : } x$$
$$(107.88) \quad (169.89)$$

x , the weight of AgNO_3 required, is found to be 15.75 grams.

6. Designation by Percentage by Weight. Occasionally a roughly prepared solution is called for on a percentage basis, and such a solution can be made quickly by dissolving the requisite weight of solute in the desired volume of water. Thus, a 5 per cent solution of AgNO_3 is usually (though erroneously) made to contain 5 grams of AgNO_3 in 100 ml. of water. This of course is not a true weight relationship; a true 5 per cent solution of AgNO_3 is one made by dissolving 5 grams of AgNO_3 in 95 grams of water.

The strength of the concentrated acids and NH_4OH used in the laboratory is expressed on a percentage basis as well as by means of the specific gravity. For example the "concentrated" HCl solution contains 37.33 per cent by weight of the pure solute. Computations involving reagents of this type are illustrated later by examples and problems in conjunction with the specific-gravity designation.

7. Designation by Means of Specific Gravity. This important property of a solution is employed particularly for the common acids and NH_4OH . By specific gravity is meant the weight of a given volume of liquid compared to the weight of an equal volume of water. Specifically, a solution of hydrochloric acid of specific gravity 1.10 is 1.10 times heavier than water. A milliliter of this solution therefore weighs 1.10 grams. This solution contains 20 per cent of pure HCl by weight (see specific-gravity table, Appendix, page 374). A milliliter of this solution will contain 1.10×0.20 or 0.220 gram of pure solute.

8. Volume-Ratio Designation. The four dilute reagents prepared according to instructions in the laboratory by the student are designated by the ratio of the volume of concentrated reagent to the volume of water of dilution. Although the method of preparation is simple and rapid, one does not know, until a calculation has been made, just how much pure solute is present. An example will show how such a computation is made.

Example 3. A 1:2 HCl solution, such as made in the laboratory by diluting 10 ml. of concentrated HCl with 20 ml. of water, contains what weight, in grams, of pure HCl?

Referring to the specific-gravity table in the Appendix, we find that the concentrated acid has a specific gravity of 1.19 and contains 37.33 per cent of pure HCl by weight. Therefore one milliliter of the concentrated acid weighs 1.19 grams and contains 1.19×0.3733 or 0.444 gram. Since 10 ml. were used, the resulting mixture contains 4.44 grams of pure HCl.

If, alternatively, we wish to know the percentage by weight of pure HCl in a diluted solution, the calculation is placed on a weight basis as in example 4.

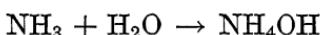
Example 4. What is the percentage of pure HCl in a solution made by diluting 10 ml. of concentrated HCl with 20 ml. of water?

The 10 ml. of acid weigh 10×1.19 or 11.9 grams. To this has been added 20 grams of water (if it is assumed that the density of water at room temperature is 1). The mixture therefore weighs $11.9 + 20.0$ or 31.9 grams. According to example 3, this contains 4.44 grams of pure HCl. Therefore the percentage of pure HCl is $4.44 \div 31.9$ or 13.92 per cent.

If further we wish to know the specific gravity of this diluted reagent, we must refer to the specific gravity table and find that a 13.92 per cent HCl solution has a specific gravity of between 1.070 and 1.065.

Before additional calculations of this type are discussed, it would be well to review the nature of these four common reagents.

Dilute ammonium hydroxide and hydrochloric, sulfuric and nitric acids are made by dilution of the concentrated solutions dispensed in the laboratory. The concentrated reagents, in turn, are manufactured by the makers of heavy chemicals, by passing gases into water. In the case of NH₄OH, ammonia gas (NH₃) is passed into water, where it reacts in accordance with the equation:



The so-called "aqua ammonia" of commerce is a solution containing the equivalent of 28.33 per cent of NH₃ by weight and has a specific gravity of 0.900. This is the "concentrated" reagent dispensed in the laboratory.

Sulfuric acid results from the chemical action of SO₃ on water:



Pure dry concentrated sulfuric acid theoretically is 100 per cent pure hydrogen sulfate. The usual concentrated laboratory reagent contains 95.60 per cent H₂SO₄ and has a specific gravity of 1.84. Concentrated H₂SO₄ will dissolve additional amounts of SO₃, resulting in fuming sulfuric acid.

Nitric acid, likewise, results from the reaction of oxides of nitrogen with water. The usual concentrated reagent contains 70.95 per cent by weight of HNO₃, and its specific gravity is 1.425.

Hydrochloric acid, however, is a saturated solution of the gas

in water. The concentrated laboratory reagent has a specific gravity between 1.175 and 1.185 and contains between 34.42 and 36.31 per cent of HCl by weight.

Example 5. Suppose it is desired to prepare a dilute hydrochloric acid solution for laboratory use, by diluting 300 ml. of the concentrated reagent (specific gravity 1.185, containing 36.31 per cent of HCl by weight) so that the dilute solution will have a specific gravity of 1.120.

The problem is to find the amount of water to be added. Since the specific gravity of the concentrated solution is 1.185, 1 ml. of this solution weighs 1.185 grams, and the total weight of the reagent is

$$300 \text{ ml.} \times 1.185 = 355.5 \text{ grams}$$

Of this weight 36.31 per cent is pure HCl (hydrogen chloride, the solute). Therefore

$$300 \times 1.185 \times 0.3631 = 129 \text{ grams}$$

In the 300 ml. of concentrated reagent there are therefore 129 grams of pure HCl. This quantity remains constant during the dilution process. Reference to the table of specific gravity of strong acids in the Appendix shows that the diluted reagent must contain 23.82 per cent of HCl by weight; that is, 23.82 per cent of the weight of the original solution, 355.5 grams, plus the weight of water added, should equal 129 grams. Let x represent the weight of water to be added, and the problem then is formulated thus:

$$300 \times 1.185 \times 0.3631 = [(300 \times 1.185) + x]0.2382$$

$$129 = (355.5 + x)0.2382$$

$$x = 186 \text{ grams} \approx 186 \text{ ml. of water}$$

Therefore the 300 ml. of the original solution should be diluted with 186 ml. of water.

It is to be noted that problems of this kind are solved on a weight basis and that the equation is based on the weight of pure solute in the original and final solution. Attention should be called to the fact that the final mixture is not equal to the sum of the volumes of the separate solutions; in example 5, the volume resulting from mixing 300 ml. of acid with 186 ml. of water will not be 486 ml. but an amount somewhat less than this.

The data given in this problem included both the specific gravity and the per cent by weight of solute for both the original and the

final solution. In case only the percentage composition or the specific gravities are specified, reference must be made to specific-gravity tables. Example 6 will illustrate the use of such tables.

Example 6. How much water must be added to 50 ml. of a nitric acid solution having a specific gravity of 1.420 in order to prepare a dilute solution having a specific gravity of 1.120?

Reference to the table of densities of strong acids in the Appendix shows that nitric acid of specific gravity 1.420 contains 69.77 per cent of HNO_3 by weight, and the required solution of specific gravity 1.120 contains 20.22 per cent of HNO_3 by weight. The problem now can be formulated as before:

$$50 \times 1.420 \times 0.6977 = [(50 \times 1.420) + x]0.2022$$

from which, when we solve for x , we find that 174 grams, equal to 174 ml., of water must be added.

In mixing solutions of two different concentrations, the method of calculation is the same in principle. The method is illustrated in example 7.

Example 7. What will be the percentage of NH_3 by weight in the mixture resulting when 50 ml. of ammonium hydroxide containing 28.33 per cent of NH_3 is mixed with 50 ml. of ammonium hydroxide containing 5.80 per cent of NH_3 by weight?

Reference to the table of densities of ammonia solutions in the Appendix shows that a solution containing 28.33 per cent of NH_3 has a specific gravity of 0.900 and one containing 5.80 per cent of NH_3 has a specific gravity of 0.976.

Let x represent the resulting percentage by weight of the mixed solution; the equation then is

$$(50 \times 0.900 \times 0.2833) + (50 \times 0.976 \times 0.058) \\ = [(50 \times 0.900) + (50 \times 0.976)]x$$

from which $x = 0.1661$. The mixture therefore contains 16.61 per cent of NH_3 .

QUESTIONS AND PROBLEMS—SET 1. REAGENTS

1. Distinguish by definition and examples: molar, molal and normal solution. What advantages are there in the use in the laboratory of "test solutions"?
2. Using a hydrochloric acid solution of a specified strength as illustration, show the relation between the designations: empirical, volume-ratio, percentage by weight and specific gravity.

INTRODUCTION

3. Calculate the grams of metallic element contained in the given weights of the following compounds:

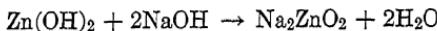
- (a) 169.888 grams of AgNO_3
- (b) 106.869 grams of $\text{Fe}(\text{OH})_3$
- (c) 137.38 grams of MgNH_4PO_4

Ans. (a) 107.88
(b) 55.84
(c) 24.32

4. Calculate the weight in grams of the following salts which are required to make liter quantities of "test solutions" such that each milliliter will contain 10 milligrams of the metallic constituent:

- (a) KNO_3
- (b) $\text{Ni}(\text{NO}_3)_2$
- (c) $\text{Bi}(\text{NO}_3)_3$

5. How much NaOH is required to dissolve 0.0523 gram of $\text{Zn}(\text{OH})_2$ according to the following reaction?



Ans. 0.0421 gram

6. What weight of reactant is required to react completely with the weights of substances listed in the following?

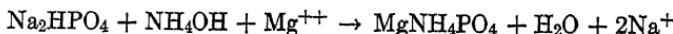
Substance	Weight, Grams	Reactant	Product
(a) AgNO_3	0.10	HCl	AgCl
(b) $\text{Cu}(\text{NO}_3)_2$	1.50	H_2S	CuS
(c) BaCl_2	1.00	$(\text{NH}_4)_2\text{CO}_3$	BaCO_3
(d) NaOH	5.00	HCl	NaCl

7. Calculate the weight of (a) H_2PtCl_6 , (b) $\text{Na}_3\text{Co}(\text{NO}_2)_6$, (c) HClO_4 , required to precipitate 1 milligram of potassium, based on the following reactions:

- (a) $\text{H}_2\text{PtCl}_6 + 2\text{K}^+ \rightarrow \text{K}_2\text{PtCl}_6 + 2\text{H}^+$ *Ans.* (a) 5.243 milligrams
- (b) $\text{Na}_3\text{Co}(\text{NO}_2)_6 + 2\text{K}^+ \rightarrow \text{K}_2\text{NaCo}(\text{NO}_2)_6 + 2\text{Na}^+$ (b) 5.167 milligrams
- (c) $\text{HClO}_4 + \text{K}^+ \rightarrow \text{KClO}_4 + \text{H}^+$ (c) 2.569 milligrams

8. How much $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ should be contained in a liter of the reagent if 1 ml. is to precipitate 0.0500 gram of BaCrO_4 ?

9. What volume of disodium phosphate solution, containing 60 grams of $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ per liter, would be required to precipitate as MgNH_4PO_4 the magnesium contained in 1 ml. of test solution? 1 ml. = 1 milligram of Mg^{++} . The reaction is



Ans. 0.25 ml.

10. What volume of ammonium sulfate reagent, containing 10 grams per 100 ml. of solution, will be required to precipitate completely the strontium, as SrSO_4 , contained in one drop (0.05 ml.) of strontium test solution? 1 ml. of test solution = 1 milligram of Sr^{++} ion.

11. The concentrated nitric acid usually supplied to the qualitative analysis laboratory contains 69.77 per cent by weight of pure HNO_3 and has a specific gravity of 1.420. What weight of pure HNO_3 is contained in (a) 1 liter, (b) 5 ml.?

Ans. (a) 990.7 grams
(b) 4.950 grams

12. What weight of NH_3 is contained in 15 ml. of ammonium hydroxide which has a specific gravity of 0.982 and contains 4.30 per cent of NH_3 by weight? To what weight of NH_4OH does this correspond?

13. If 2.5 ml. of concentrated HCl (specific gravity 1.19, containing 37.23 per cent by weight of HCl) are diluted to 100 ml., what is the concentration of HCl per milliliter?

Ans. 0.0011 gram

14. How much water must be added to 100 ml. of concentrated HNO_3 (specific gravity 1.42, containing 69.77 per cent of HNO_3 by weight) to give a reagent of specific gravity 1.20, containing 30.11 per cent of HNO_3 by weight?

15. If you are to prepare a hydrochloric acid solution of specific gravity 1.12, containing 23.82 per cent HCl by weight, how much water should you add to 200 ml. of solution which contains 30.55 per cent by weight of HCl (specific gravity 1.155)?

Ans. 64.5 ml.

16. How many milliliters of NH_4OH (specific gravity 0.900; 28.33 per cent NH_3 by weight) are required to neutralize 10 ml. of H_2SO_4 (specific gravity 1.20; 27.32 per cent H_2SO_4 by weight)?

17. How many milliliters of ammonium hydroxide containing 28.33 per cent by weight of NH_3 (specific gravity 0.900) are required to neutralize 2.5 ml. of HCl solution of specific gravity 1.19, containing 37.23 per cent HCl by weight?

Ans. 2.03 ml.

18. The concentrated ammonium hydroxide supplied to the laboratory has a specific gravity of 0.900 and contains 28.33 per cent NH_3 by weight. What is the equivalent weight of NH_4OH contained in 50 ml. of this reagent?

19. How much hydrochloric acid of specific gravity 1.19, containing 37.23 per cent HCl must be added to 50 ml. of hydrochloric acid of specific gravity 1.08, containing 16.15 per cent HCl to give a solution of specific gravity 1.13?

Ans. 38.4 ml.

20. If 75 ml. of concentrated nitric acid (specific gravity 1.420, containing 69.77 per cent HNO_3 by weight) are mixed with 50 ml. of nitric acid of specific gravity 1.200, containing 32.34 per cent HNO_3 , what percentage by weight of HNO_3 will the mixture contain?

CHAPTER II

THE THEORY OF SOLUTIONS. THE ANALYTICAL GROUPING OF THE COMMON ELEMENTS. THE ALKALI METALS

THE THEORY OF SOLUTIONS

When a small amount of sugar or sodium chloride is added to water, the solid disappears in the liquid, forming a homogeneous mixture which is called a solution. All solids show a tendency to dissolve in liquids, the amount of different solids taken up by a given amount of liquid varying between wide limits. Liquids also may dissolve in solids or in other liquids. Gases too show this property of dissolving in liquids and in solids. Thus it is possible to have solutions consisting of solids, liquids, and gases dissolved in liquids, as well as solids, liquids and gases dissolved in solids.

The component that is present in greater amount is referred to as the solvent, and the other component is known as the solute. Thus, in a solution of sugar in water, the sugar is the solute and the water the solvent. Water is the commonest solvent used, and throughout qualitative analysis we deal largely with aqueous solutions. Solid inorganic substances are the chief solutes, although gases and liquids are solutes in some cases.

A true solution is one in which the solute is disintegrated down to at least molecular dimensions and uniformly distributed throughout the solvent. However, we may have uniform distribution of a substance in a liquid in which the dispersed substance consists of aggregates of molecules; colloidal suspensions are of this type. The colloidal state is discussed more fully on page 349. Throughout this book, the word solution will be used to designate true solutions, and, in fact, aqueous solutions will be implied thereby.

Limits of Solubility. The extent to which the solute will be taken up by a given amount of solvent under definite specified conditions is a characteristic property of the substance. The amounts of different substances which will dissolve in a definite quantity of water, such as one liter, vary considerably. A solu-

tion is said to be saturated when the dissolved material is in equilibrium with an excess of undissolved solute. Inasmuch as these differences in solubility constitute a most useful means in qualitative analysis of separating one substance from another, the study of solubility relationships and the selection of reactions which will differentiate substances on the basis of their solubilities become very important.

If more than the saturation amount of solid is added to a solvent, the excess will remain as undissolved solid, except in those cases where supersaturated solutions result in an unstable condition. An idea of the wide variation in the amounts of different solid solutes required for saturated solutions can be gained by reference to solubility tables. The solubility of a solid in water increases, as a general rule, with increase in temperature and only slightly with increase in pressure. An important application of the general equilibrium theory involving saturated solutions of slightly soluble substances (precipitates) is discussed in Chapter III and is known as the solubility-product principle.

Two liquids may be totally or only partially soluble in each other. Thus water and alcohol mix in all proportions, and no limit can be placed on the saturation amount. Carbon tetrachloride is only slightly soluble in water and, if the solubility is exceeded, the excess will remain as a second-liquid layer; we speak of these two liquids as being practically immiscible in each other. Chloroform, ether, benzene and many other organic liquids form similar two-liquid layer systems with water.

The amount of a gas which will dissolve in a definite volume of water under existing temperature and pressure conditions too is fixed by its saturation quantity, and any excess escapes as free gas. In general, the solubility decreases with rise in temperature and increases with an increase in pressure. Some gases, such as hydrogen sulfide, merely dissolve in water, whereas others, such as sulfur trioxide and ammonia, react with water. The solutions of gases in water, whether or not reaction takes place with the solvent, comprise some of our most important and commonest reagents.

Properties of Aqueous Solutions. Experiment shows that many of the properties of water are altered considerably when dissolved material is present. Thus, pure water freezes at $0^{\circ}\text{ C}.$, boils at $100^{\circ}\text{ C}.$ under 1 atmosphere of pressure and exerts a vapor pressure of a definite magnitude at any specified temperature. But when,

for example, sugar or sodium chloride is added to water, the freezing point of the water is lowered, the boiling point is raised and the vapor pressure is lowered, the extent of the change in these properties varying with the quantity and nature of the solute present. The osmotic pressure of the solution too increases with increased concentration. These changes in vapor pressure, freezing and boiling points and osmotic pressure are all interrelated, and, if one is known, the others can be calculated. Hence, we shall frequently discuss the effect of various conditions on one or two of these quantities, implying but not mentioning the corresponding changes in the others.

Solutes may be divided into two general classes, electrolytes and non-electrolytes, according to the behavior of their aqueous solutions. Compounds such as sugar, glycerol, urea and organic compounds in general are non-electrolytes. If compounds of this type are dissolved in such amounts that the ratio of the number of solute molecules to the number of water molecules in the solution is the same for the different solutions, the same freezing-point lowering and the same boiling-point rise will be produced in each case. Thus, one gram-molecular weight (one mole) of any non-volatile non-electrolyte dissolved in 1000 grams of water will lower the freezing point 1.86° C. and raise the boiling point 0.52° C. In such a solution there will be $1000 \div 18.016 = 55.51$ moles of water to 1 mole of solute or, since a mole of any substance represents a definite number of molecules [Avogadro's number, 6.023×10^{23}]—this value supplants the previous value of 6.06×10^{23} : see *Birge, Rev. Modern Phys.*, (13, 233 (1941)], this solution will contain 55.51 water molecules for each solute molecule. It is to be emphasized that the ratio between the number of solvent molecules and solute particles is the important factor in determining the effect of a solute on the freezing and boiling points.

Solutions of non-electrolytes, as the term suggests, are very poor conductors of electricity. Electrolytes, on the other hand, contain bonds that are easily broken by the attraction of the solvent molecules when the compound is dissolved. Solutions of electrolytes readily conduct an electric current and exhibit greater deviations in freezing and boiling points than non-electrolyte solutions of the same molecular concentration, that is, the same number of moles of solute per 1000 grams of solvent.

The Phenomenon of Ionization. To explain the abnormal behavior of dissolved acids, bases and salts, Arrhenius, in 1885, pro-

posed the theory of ionization. This assumes that, when acids, bases and salts are dissolved in certain liquids, particularly water, the molecules of the solute dissociate or ionize to a greater or lesser extent into positively and negatively charged particles called ions, those bearing positive charges being called cations and those with negative charges anions. Compounds showing this behavior are called electrolytes. The extent of the dissociation depends upon the nature of the solute, the concentration, the temperature and the solvent. The ions behave as independent units, irrespective of the nature of the compound from which they are derived, and, when two solutions of electrolytes react, they show the behavior only of the constituent ions. The phenomenon of ionization can be considered as a reversible chemical reaction between the dissolved non-ionized molecules and the cations and anions resulting therefrom.

If the extent to which different acids, bases and salts ionize is compared for solutions containing equal gram-molecular weights of the solute at the same temperature, it will be found that ionization varies considerably with different electrolytes. Electrolytes in moderately dilute solutions, in which the proportion of the ionized to the non-ionized part is large, are strong electrolytes. Examples of strong electrolytes are solutions of HCl, NaOH, NaCl and, as a general rule, most inorganic salts. On the other hand, weak electrolytes are those in which the tendency to ionize in moderately dilute solutions is relatively small, such as solutions of NH₃, HC₂H₃O₂, H₂S, H₂CO₃ and water itself (See Table XI in Chapter V).

Polar and Non-Polar Solvents. The ionizing action of water as a solvent may be explained on the basis of the asymmetry of the water molecule. The water molecule is correctly represented not by a linear formula, H—O—H, but rather by a formula of the



type H-----+-----H in which the angle HOH is approximately 100°. As a result of the asymmetry, the "centers of gravity" of the positive and negative charges do not coincide as they would if the three atoms lay in a straight line; consequently, the molecule acts like a tiny magnet: that is, it is a polar compound and constitutes a polar solvent. Any other compound, such as NH₃, with a similar lack of symmetry will constitute a polar solvent.

When a polar but non-ionized solute is placed in a polar solvent the solvent molecules attach themselves to the solute and by their attraction tend to split the molecule into ions.

In this connection it should be pointed out that if a polar but non-ionized substance like HCl is dissolved in a non-polar solvent, benzene for example, it is a non-electrolyte. This emphasizes again the important effect of the solvent in determining the properties of the solute in a solution.

The Debye-Hückel Theory. We have mentioned previously the abnormal effect of electrolytes on the freezing and boiling points and other properties of solutions. According to the Arrhenius theory of ionization, an ion has the same ability, for example, to lower the freezing point as a non-ionized molecule. Hence, if a molecule divides into 2 ions, 1 gram-molecular weight of the substance in 1000 grams of water should produce a lowering of twice 1.86° C., provided the substance is completely ionized. Ordinarily, however, the lowering actually measured is somewhere between 1.86° C. and $2 \times 1.86^{\circ}$ C. for a substance giving 2 ions per molecule, and somewhere between 1.86° C. and $3 \times 1.86^{\circ}$ C. for a substance giving 3 ions per molecule. Arrhenius interpreted this behavior as indicating incomplete dissociation of the solute and calculated the percentage of ionization which would have to occur to account for the experimental results. This explanation seemed to be supported by the observation that, when a solution of an electrolyte is diluted, the calculated degree of ionization increases until in very dilute solutions it approaches or even reaches 100 per cent.

Since most salts in the solid state consist exclusively of ions, it is reasonable to suppose that they also would be ionized completely in solution. If such is the case some other explanation must be found for the experimental observation that, except in very dilute solutions, the freezing-point lowering is less than it would be if each ion had the same effect as a non-ionized molecule. This difficulty exists only for strong electrolytes; weak electrolytes are admittedly incompletely ionized, and the Arrhenius theory is directly applicable to them.

To account for the behavior of strong electrolytes Debye and Hückel developed mathematically a theory which assumes complete ionization of strong electrolytes in solution. Simply expressed, this theory states that, in the immediate neighborhood of any cation, there are more anions than cations, and near any anion

there are more cations than anions. This may be attributed to the well-known fact that opposite charges attract and like charges repel. A somewhat similar situation exists in salt crystals. In NaCl, for example, each sodium ion is surrounded at equal distances by 6 chloride ions, and each chloride ion is likewise surrounded by 6 sodium ions. Consideration of such a crystal may aid in visualizing the situation existing in a solution, but it must be remembered that in the solution the ions are free to move, and the number as well as the distances of the surrounding ions are by no means definite.

The effect of the "cloud" or "atmosphere" of ions surrounding a particular ion is to restrict the motion of the ion in question, for motion of the ion will be opposed by the attraction of the oppositely charged ionic atmosphere. This restriction of motion manifests itself as a decreased activity of the ion; that is, the ion will have less effect in lowering the freezing point than it would have if its motion were unopposed by oppositely charged ions. As the solution is diluted, the distances between the ions become greater, thus decreasing the effect of the ionic atmosphere and allowing the ions to exhibit their full influence on the freezing and boiling points. For very dilute solutions the Debye-Hückel and Arrhenius theories are equivalent.

The change produced in the conductivity and related properties when a solution of a strong electrolyte is diluted may be explained in either of two ways: (1) the mobility or freedom of motion of the ions may remain constant but the number of ions may increase, owing to the dissociation of non-ionized solute molecules; (2) the number of ions may remain constant (since there are no non-ionized solute molecules present), but the mobility of the ions may increase, owing to a decreased interference from the ionic atmosphere surrounding each. The first assumption is made in the development of the Arrhenius theory, and the second underlies the Debye-Hückel theory. The first condition applies to weak electrolytes and the second to strong electrolytes.

To take into account the experimental fact that strong electrolytes appear to be incompletely ionized, as judged by their effect on vapor pressures, and the like, a term called the activity or effective concentration is introduced. Numerically, the activity of a molecule or ion in a given solution is equal to the concentration that it would have to have to give the observed effect on the vapor pressure if each molecule or ion had the same effect that it has in a

very dilute solution. The activity is related to the concentration by the expression,

$$a = fC$$

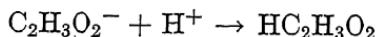
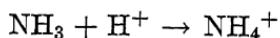
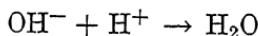
where f is a fraction called the activity coefficient.

The activity coefficient is similar in many respects to the degree of ionization used in connection with weak electrolytes. It increases with the dilution and becomes equal to 1 in very dilute solutions. It is decreased by the addition of ions other than the ones under consideration; one result of this behavior is the so-called "salt effect."

The experimental determination of activities and activity coefficients is not easy. Moreover, owing primarily to the difficulty of securing appropriate data, activities do not lend themselves so readily to elementary calculations as do concentrations. It should be realized that, even for weak electrolytes and non-electrolytes, activities must be used instead of concentrations if perfect accuracy is desired. The common failure to do this sacrifices a small amount of accuracy for a considerable gain in simplicity.

Acids and Bases. An acid is a substance (molecule or ion) having the chemical property of losing a proton to another substance. Since a proton is the same as a hydrogen ion, we also can say that an acid is a substance that is able to furnish hydrogen ions. This includes all the compounds such as HCl, HNO₃, HC₂H₃O₂, which commonly have the term "acid" included in their names, as well as certain other substances such as HCO₃⁻, NH₄⁺, H₂O, which usually are not thought of as being acids. Acids are said to be monoprotic, diprotic, triprotic, and so on, according to their ability to furnish 1, 2, 3 or more protons per molecule.

A base is a substance (molecule or ion) which has the chemical property of gaining a proton from another substance. In this classification are included such substances as hydroxyl ion, ammonia, acetate ion and the like, since they are able to combine with hydrogen ions as indicated by the equations:



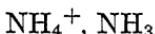
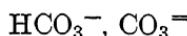
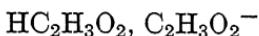
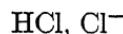
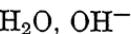
One of the chief points of difference between the traditional and the modern idea of acids and bases is the concept of a base. Ac-

cording to the traditional theory, a substance is a base if and only if it provides hydroxyl ions. The modern theory states that it is not the substance that provides the hydroxyl ion but the hydroxyl ion itself that is the base. Thus, NaOH is not a base, but it contains the base, OH^- . Moreover, there are many bases other than the hydroxyl ion, as already indicated. Compounds such as NaOH which furnish a high concentration of hydroxyl ions we call alkalies.

A consideration of the definitions will indicate that every acid is related to some particular base in a definite way. This relationship is indicated by the general equation,



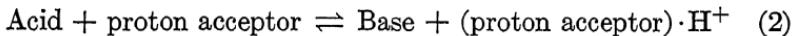
that is, the substance remaining after the removal of a hydrogen ion from an acid is a base. It will be noticed that the forward reaction provides the definition of an acid, whereas the definition of a base depends on the reverse reaction. An acid and a base that are related in the way indicated by the equation are called a conjugate pair. Some examples of conjugate pairs are the following, the acid being mentioned first:



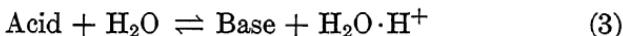
Our definition states that an acid must be capable of losing a proton to another substance. This implies that the proton is transferred from one acid to some proton acceptor and that therefore the simple equation,



is incomplete and might better be written



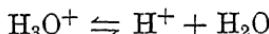
This indicates that in solutions the protons are always present in combination with some other ion or molecule and never exist in the form of simple hydrogen ions. The solvent itself frequently functions as a proton acceptor, so that equation 2 may be rewritten for aqueous solutions in the following form:



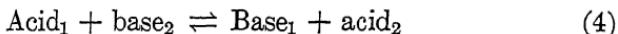
The ion $\text{H}_2\text{O} \cdot \text{H}^+$ or H_3O^+ is called the hydronium or oxonium ion

and, owing to the action indicated by the equation, is present in all aqueous acid solutions. This is not a "theoretical" statement; the actual existence of H_3O^+ ions is indicated by many types of experimental evidence which, however, because of its complexity, cannot be described here.

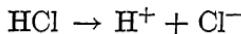
Consideration of equation (2) leads to a very simple observation. The substance that we have designated as "proton acceptor" agrees with the definition of a base since it accepts protons from the acid. Also, the H_3O^+ ion satisfies the requirement for an acid since the equation,



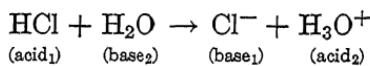
describes its nature. The conclusion is that any acid-base reaction really involves two acids and two bases, that is, two conjugate pairs. The most general equation then is of the type



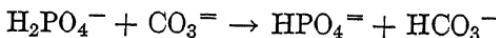
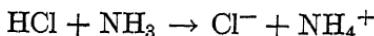
where $(\text{acid}_1, \text{base}_1)$ and $(\text{acid}_2, \text{base}_2)$ are conjugate pairs. For example, the reaction which is usually written as



is in reality



Of course, the solvent is not necessarily included in the equation since some other proton acceptor may be present, as the following equations show:



Hydration of Ions. When we consider the hydronium ion, H_3O^+ , as a hydrated hydrogen ion it must not be supposed that hydration is peculiar to the hydrogen ion. All ions in water solution probably are hydrated—to an indefinite and unknown extent, to be sure—and might be represented as $\text{Na}(\text{H}_2\text{O})_x^+$, $\text{Cl}(\text{H}_2\text{O})_y^-$ and so on. Since the extent of the hydration is unknown, and since the inclusion of the water in the formula of the ion contributes little to our knowledge of the properties of the ion, we shall omit it entirely in subsequent discussions. When we look at the formula of an ion, however, we shall remember that the ion really is hydrated and that the formula, although it tells the truth, does not tell the whole truth.

The situation in the case of the hydronium ion is, however, somewhat different. Because of its very small size—approximately 1/100,000 of the diameter of an ordinary atom—the proton probably is buried within or is surrounded by a single water molecule. This means that, although it is conceivable that the proton may be attached to a number of water molecules, the probability is great that it is associated with only one, and therefore the degree of hydration is somewhat less indefinite than it is for any other ion. Moreover, as mentioned previously, H_3O^+ ions have been definitely identified in some compounds. But now, having justified a belief in the existence of H_3O^+ ions, we shall, for simplicity, henceforth omit the water from our written formulas, just as we do with the other hydrated ions. The symbol, H^+ , will suggest, however, that what we are really talking about is the hydrated proton, more completely represented by H_3O^+ .

The Concentration of Solutions. In Chapter I were described the various ways or systems in common use for designating the strength of solutions. Among the systems employed is the molar system, in which the concentration is expressed in gram moles of solute per liter of solution. The unit of mass or quantity is the gram mole, when referring to the amount of solute. When referring to the ions into which the solute dissociates, the term gram ion is frequently employed, and when referring to the atomic weight of an element, the corresponding term gram atom is the appropriate designation. The units of mass are employed in calculations dealing with the Law of Chemical Equilibrium and must be understood before equilibrium theory is introduced. Gram-mole and gram-ion quantities and concentrations are here defined and illustrated by numerous examples and problems.

Gram-Atom, Gram-Mole and Gram-Ion Quantities. A gram-atom or a gram-atomic weight of an element is a weight in grams equal to the atomic weight of that element. Thus, a gram atom of silver consists of 107.88 grams of silver, since this number is the atomic weight of silver. Likewise 35.457 grams of chlorine is one gram atom of chlorine, and 1.008 grams of hydrogen a gram atom of hydrogen. One half of the atomic weight of an element in grams constitutes one half of a gram atom; one tenth of the atomic weight in grams, a tenth of a gram atom, and so on.

A gram mole or a gram-molecular weight (sometimes simply called a mole) is the molecular weight of a substance in grams. One gram mole of AgCl, for example, consists of 143.337 grams of

this compound, this number being the molecular weight of AgCl. A gram mole of HCl weighs 36.465 grams, and a gram mole of NaOH 40.005 grams. One half of the molecular weight is a half-mole, and one tenth of the molecular weight constitutes 0.1 gram mole. Thus 0.5 of 36.465 or 18.233 grams of HCl is 0.5 gram mole of HCl, and 3.647 grams of HCl is 0.1 gram mole of HCl.

A gram ion is the atomic or molecular weight of the ion in grams; that is, if the ions in a solution consist of charged *atoms*, such as Ag⁺, H⁺, Cl⁻, the atomic weight in grams of the element in question constitutes one gram ion; and, if the ions consist of *charged groups of atoms* such as the ammonium ion, NH₄⁺, the nitrate, NO₃⁻, the sulfate, SO₄⁼ or the acetate, C₂H₃O₂⁻, ion, the molecular weight of the charged radical, in grams, constitutes 1 gram ion. If, for example, a solution of HCl contains 1.008 grams of H⁺ ion and 35.457 grams of Cl⁻ ion, there are present 1 gram ion of hydrogen ion and 1 gram ion of chloride ion. Or, again, if a certain solution is made by dissolving one gram-molecular weight of AgNO₃ in water and the resulting solution is completely ionized into Ag⁺ ions and NO₃⁻ ions, the solution will contain 1 gram ion of Ag⁺ ion (107.88 grams) and 1 gram ion of NO₃⁻ ion (62.008 grams).

It is obvious that the three terms *gram atom*, *gram mole* and *gram ion* are fundamentally alike and define the same kind of unit of measurement, differing only in that they refer to different conditions of matter. The gram atom refers to the atomic state of an element, the gram mole to a compound or uncharged radical and the gram ion to an ionized atom or radical. This distinction is one of exact definition rather than of any real difference in meaning.

These are the units of mass used in all equilibrium calculations; they must be understood thoroughly before computations of equilibria are undertaken. A great deal of the difficulty which students have with equilibrium calculations is traceable directly to an improper or incomplete understanding of these fundamental units. A few illustrative typical examples follow.

Example 1. What gram-mole quantity is represented by 5.846 grams of NaCl?

The atomic weight of Na is 23.00 and that of Cl is 35.46, the molecular weight of NaCl being therefore 58.46. Dividing the weight in grams by the molecular weight gives the gram-molecular weight:

$$\frac{5.846 \text{ (weight in grams)}}{58.46 \text{ (molecular weight)}} = 0.1000$$

The mass represented in the problem is therefore 0.1 gram mole.

Example 2. What gram-atom quantities of sodium and of chlorine are contained in 5.846 grams of NaCl?

Two methods of solution are possible. We may find, by direct proportion, the weight in grams of sodium and chlorine contained in the given weight of NaCl:

$$\text{Na:NaCl} = x:5.846$$

$$\text{Cl:NaCl} = y:5.846$$

$$x = 2.300$$

$$y = 3.546$$

Thus we find that 5.846 NaCl is composed of 2.300 grams of Na and 3.546 grams of Cl. Dividing the gram weights by the atomic weights of Na and Cl, respectively, gives the required gram-atom quantities,

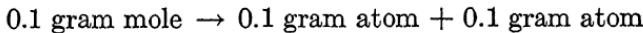
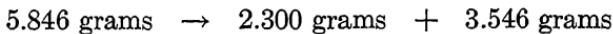
$$\frac{2.300}{23.00} = 0.1000 \text{ gram atom of Na}$$

and

$$\frac{3.546}{35.46} = 0.1000 \text{ gram atom of Cl}$$

This method is roundabout and unnecessarily involved; it is given only to show the contrast with the following simple method.

The more direct, logical and sensible method is to find first the gram-mole quantity represented. This is, as in example 1, 0.1 of a gram mole. Then, since a molecule of the compound in question is composed of 1 atom of Na and 1 atom of Cl, the mass of 0.1 gram mole will consist of 0.1 gram atom of Na and 0.1 gram atom of Cl. This relationship can be verified by referring to the calculations used in the first method, and is shown in the scheme:



Example 3. What are the gram-ion quantities of Na^+ ion and of Cl^- ion if 5.846 grams of NaCl are dissolved in sufficient water so that the ionization may be considered 100 per cent complete?

The reaction of ionization is



Since 5.846 grams of the solute constitute 0.1 gram mole, the solute

consists, as shown in example 2, of 0.1 gram atom each of Na and Cl. The atoms now bear charges and are ions. Hence the solution contains 0.1 of a gram ion of Na^+ ion and 0.1 of a gram ion of Cl^- ion.

If two or more atoms of the same element are present in a compound, the calculation is made as in the following example.

Example 4. What gram-ion quantities of Ca^{++} and of Cl^- are contained in 1 gram mole of CaCl_2 if complete ionization of the dissolved solute is assumed?

Since 2 ions of chlorine are present for each ion of calcium, there are present in 1 gram mole of the compound 1 gram ion of Ca and 2 gram ions of Cl.

From these examples it follows that to convert gram quantities into the corresponding gram-mole units, the given weight in grams is divided by the molecular weight of the compound or radical. The conversion formula is

$$\frac{\text{Weight in grams}}{\text{Molecular weight}} = \text{Gram moles}$$

To convert gram-mole quantities into gram weights the given gram-molecular quantity is multiplied by the molecular weight. Expressed as an equation, the formula becomes

$$\text{Gram moles} \times \text{molecular weight} = \text{Weight in grams}$$

Conversion from gram quantities to gram-ion quantities is made, as with gram-mole units, by dividing the weight in grams by the atomic or molecular weight of the ion in question. Conversely, to go from gram-ion units to gram quantities, the given gram-ion quantity is multiplied by the atomic weight of the charged atom or by the molecular weight of the charged radical.

In dealing with solutions of electrolytes, the degree of ionization of the solute must be taken into consideration. For dilute solutions of strong electrolytes, the ionization may be assumed to be complete. When the amount of solute and the percentage of ionization are known, it is an easy matter to calculate the mass of ions and of non-ionized solute present. The values may be expressed in terms of gram ions and gram moles or in terms of grams. Without introducing, for the present, the complication that arises from the volume of solution involved, the total amount of ionized and non-ionized solute may be readily expressed in the preceding units. Examples 5 and 6 will make this clear.

Example 5. What gram-ion quantities of Na^+ ion and Cl^- ion and gram-mole quantity of NaCl are contained in a solution made by dissolving 0.050 gram mole of NaCl in water, the resulting solution being 95.0 per cent ionized?

In this solution 95.0 per cent of the solute has ionized according to the reaction



leaving 5.00 per cent non-ionized. The total amount of solute is 0.050 gram mole. Therefore the solution contains

$$0.050 \times 0.95 = 0.0475 \text{ gram ion of } \text{Na}^+ \text{ ion}$$

$$0.050 \times 0.95 = 0.0475 \text{ gram ion of } \text{Cl}^- \text{ ion}$$

$$0.050 \times 0.05 = 0.0025 \text{ gram mole of non-ionized NaCl}$$

Example 6. If, in example 5, the gram quantities are desired, the simplest method is to multiply the calculated quantities by the atomic weights of the ions and the molecular weight of the salt, respectively.

$$0.0475 \times 23.00 = 1.093 \text{ grams of Na as } \text{Na}^+ \text{ ion}$$

$$0.0475 \times 35.46 = 1.684 \text{ grams of Cl as } \text{Cl}^- \text{ ion}$$

$$0.0025 \times 58.46 = \underline{0.146 \text{ gram of non-ionized NaCl}}$$

$$2.923 \text{ grams of total solute}$$

A solution containing 0.050 gram mole of NaCl contains 0.050 \times 58.46 or 2.923 grams of dissolved NaCl , thus accounting for the total amount of solute.

Molar and Gram-Ion Concentration. In the preceding discussion of gram-mole and gram-ion quantities no specific reference has been made to the volume of solution which contains the certain specified amount of solute. It is important, in dealing with reactions and with equilibrium relationships in solutions, that the concentration of the solutions be specified with respect to the gram-molar and gram-ion quantities present in the volume of solution under consideration.

If a gram-molecular weight of substance as solute be taken, it is possible to go about dissolving it in four ways:

1. A gram mole dissolved in the solvent and the solution made up to 1000 ml.
2. A gram mole dissolved in the solvent and the solution made up to 1000 grams.

3. A gram mole dissolved in 1000 ml. of the solvent.
4. A gram mole dissolved in 1000 grams of solvent.

A solution made up according to method 1, that is, one containing a gram-molecular weight of the solute per liter of *solution*, is known as a *molar solution*. A solution containing a gram-molecular weight in 1000 grams of solvent is a *molal solution*. It is with molar solutions and concentrations that we are concerned here.

Concentrations in Terms of Molar Units. In calculations of equilibria in chemical reactions, the amount of reacting constituents are expressed in terms of gram-mole, gram-ion or gram-atom quantities. When reactions in solutions are considered, the quantities are referred to a liter basis. *The concentration of a solution is defined as the amount of solute present in a liter of solution.* Thus, if a certain solution contains 1 gram mole of the solute in a liter of the solution, the concentration is 1 molar (1 M) or the molarity is 1; and, if a certain other solution contains, for example, 0.0125 gram mole of solute in a liter of solution, this solution is said to be 0.0125 molar (0.0125 M), or its molarity is 0.0125. The symbol C is used in this text to indicate the concentration of a solution in terms of molarity; some authors prefer to use brackets, [], when referring to concentrations.

Confusion sometimes arises in calculations when the volume of solution is other than 1 liter. For example, suppose we are dealing with 200 ml. of a solution which contains 0.2 gram mole of solute. The actual gram-mole quantity is 0.2 of a gram-molecular weight, but the *concentration of this solution* is 1 molar, because, when this quantity is referred to a liter basis, the amount of solute corresponds to 1 gram mole per liter. Likewise, if 500 ml. of a 0.0125 M solution is involved, the concentration or molarity is 0.0125 but the gram-mole quantity (in 500 ml.) is 0.00625.

Example 7. What is the concentration of a solution which contains 0.005 gram mole of solute in 5 ml. of solution?

Since in 5 ml. there is 0.005 gram mole, in 1000 ml. there would be $0.005 \times (1000/5) = 1$. The concentration of the solution is therefore 1 molar (1 M).

Example 8. What is the molarity of a hydrochloric acid solution of specific gravity 1.12, containing 23.82 per cent of HCl by weight?

One liter of the solution contains $1000 \times 1.12 \times 0.2382 = 266.8$ grams of HCl. A molar solution of hydrochloric acid contains 36.46 grams of HCl per liter. The molarity of the solution is therefore $(266.8/36.46) = 7.32\text{ M}$.

Concentrations in Terms of Gram-Ion Units. If a part or the entire amount of the solute in a solution is ionized, the concentration of the ions is expressed in gram-ion units. Thus, if a 0.1 *M* solution of NaCl (containing 0.1 gram mole or 5.846 grams of NaCl per liter of solution) is assumed to be completely ionized into sodium ions and chloride ions (actually 85.2 per cent), there are present 0.1 of 1 gram ion of Na^+ ion and 0.1 of 1 gram ion of Cl^- ion. No suitable word has been coined to express the concentration of ions corresponding to the word "molarity." We may refer to the concentrations by saying that the foregoing solution is 0.1 *M* with respect to both Na^+ ion and Cl^- ions, meaning that the concentration of both sets of ions is 0.1 gram ion, or that the gram ion concentrations are both 0.1.

In solutions in which two or more ions of one kind, in relation to one ion of another kind, are furnished by the ionization of the solute, the *total* concentration of each set of ions must be determined. For instance, in a 0.001 *M* solution of CaCl_2 , if the solution is completely ionized, there are present 0.001 gram ion of Ca^{++} ion and 0.002 gram ion of Cl^- ion, per liter of solution, the concentration of chloride ion being double that of the calcium ion. If 1×10^{-5} gram mole of Bi_2S_3 dissolves in a liter of water, this extremely dilute solution may be considered to be 100 per cent ionized and the concentrations are therefore 2×10^{-5} gram ion of Bi^{+++} ion and 3×10^{-5} gram ion of S^- ion per liter, respectively.

If solutions are known to be less than 100 per cent ionized, the gram-ion concentrations of the respective ions as well as the gram-mole concentration of that fraction of the solute which is not ionized may readily be computed.

Example 9. What are the gram-ion concentrations of acetate and hydrogen ions and the gram-mole concentration of non-ionized acetic acid, in a liter of 0.1 *M* $\text{HC}_2\text{H}_3\text{O}_2$ which is 1.34 per cent ionized?

Since there was present originally 0.1 gram mole of $\text{HC}_2\text{H}_3\text{O}_2$ and 0.0134 of the total has ionized, there are now present as ions 0.0134 of 0.1 or 0.00134 gram ion of H^+ ion, and 0.0134 of 0.1 or 0.00134 gram ion of $\text{C}_2\text{H}_3\text{O}_2^-$ ion. The remainder of the solute ($1 - 0.0134 = 0.9866$), 98.66 per cent, is not ionized; 98.66 per cent of 0.1 gram mole, 0.1×0.9866 or 0.09866 gram mole is the concentration of non-ionized $\text{HC}_2\text{H}_3\text{O}_2$.

The volume of solution concerned in an equilibrium calculation is usually less than 1 liter, and, consequently, when the gram-ion

concentrations of the ionized portions of the dissolved electrolyte are being expressed, the gram-ion quantities must be referred to a liter in order to conform with the definition of concentration.

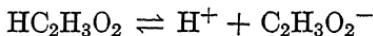
Example 10. Calculate the gram-ion concentrations of H^+ and $C_2H_3O_2^-$ ion in an acetic acid solution which is made by dissolving 0.06 gram of $HC_2H_3O_2$ in water and diluting to 10 ml., the solution being 1.34 per cent ionized.

The gram-mole quantity of solute first may be found by dividing the gram weight by the molecular weight.

$$0.06 \div 60 = 0.001 \text{ gram mole in 10 ml.}$$

(mol. wt.)

The ionization takes place to the extent of 0.0134 according to the reaction



Therefore

$$0.001 \times 0.0134 = 0.0000134 \text{ gram ion of } H^+ \text{ ion in 10 ml.}$$

$$0.001 \times 0.0134 = 0.0000134 \text{ gram ion of } C_2H_3O_2^- \text{ ion in 10 ml.}$$

In 1000 ml. there would be

$$(1.34 \times 10^{-5}) \times 1 \times 10^2 = 1.34 \times 10^{-3}$$

or

$$0.00134 \text{ gram ion of } H^+ \text{ ion}$$

and

$$(1.34 \times 10^{-5}) \times 1 \times 10^2 = 1.34 \times 10^{-3}$$

or

$$0.00134 \text{ gram ion of } C_2H_3O_2^- \text{ ion}$$

The concentration of both ions is therefore 0.00134 gram ion per liter.

A simple method of making the calculation is to refer the total solute to a liter basis directly. If in 10 ml. there is present 0.06 gram of solute, the amount in 1 liter would be 6 grams. The molarity of the solution, with respect to the solute, is therefore $6/60$ or $0.1 M$.

The gram-ion concentrations, since the solute is 1.34 per cent ionized, are as in example 9:

$$0.1 \times 0.0134 = 0.00134 \text{ or } 1.34 \times 10^{-3} \text{ gram ion of } H^+ \text{ ion}$$

and

$$0.1 \times 0.0134 = 0.00134 \text{ or } 1.34 \times 10^{-3} \text{ gram ion of } C_2H_3O_2^- \text{ ion}$$

QUESTIONS AND PROBLEMS—SET 2. MOLAR CONCENTRATIONS

1. Define the term "concentration." Distinguish among gram atom, gram mole and gram ion. Distinguish between gram-ion quantity and gram-ion concentration, using suitable examples.

2. Calculate the grams of compound represented by 0.1000 gram mole of each of the following:

- (a) H_2SO_4
- (b) $\text{Ca}(\text{OH})_2$
- (c) MgNH_4PO_4

3. What gram-ion quantities are represented by

- (a) 107.88 grams of Ag^+
- (b) 3.206 grams of S^-
- (c) 0.5584 gram of Fe^{+++}

Ans. (a) 1.0
(b) 0.1
(c) 0.01

4. What weight in grams is represented by the following quantities of ions?

- (a) 0.100 gram ion of Ag^+
- (b) 2.0 gram ions of H^+
- (c) 0.200 gram ion of Mg^{++}

5. Express the given amount of the following substances in terms of gram moles.

- (a) 143.34 grams of AgCl
- (b) 18.232 grams of HCl
- (c) 0.2915 gram of $\text{Mg}(\text{OH})_2$

Ans. (a) 1.000
(b) 0.500
(c) 0.00500

6. Express the following gram weights in terms of gram-ion units:

- (a) 1.0×10^{-4} gram of Ag^+
- (b) 1.86×10^{-6} gram of OH^-
- (c) 1.10×10^{-7} gram of H^+

7. For the following solutions, each containing 10 milligrams per milliliter of the ion specified, calculate the gram-ion quantities:

- (a) Fe^{+++}
- (b) Mg^{++}
- (c) SO_4^-

Ans. (a) 1.8×10^{-4} gram ion
(b) 4.1×10^{-4} gram ion
(c) 1.0×10^{-4} gram ion

8. Calculate the molarity of the following solutions which contain per liter the specified amounts of solute:

- (a) 3.646 grams of HCl
- (b) 20.0 grams of NaOH
- (c) 10.0 grams of BaCl_2

9. What is the gram-ion concentration of each of the following test solutions each containing 1 milligram per milliliter of the respective cation?

- (a) Na^+
- (b) Ca^{++}
- (c) Cr^{+++}
- (d) Sn^{++}
- (e) Sn^{++++}

Ans. (a) 0.0435 gram ion per liter
(b) 0.00249 gram ion per liter
(c) 0.0192 gram ion per liter
(d) 0.00842 gram ion per liter
(e) 0.00842 gram ion per liter

10. How many grams per liter of the following solution are required to make solutions of the specified molarity?

- (a) 0.1 *M* HCl
- (b) 1.0 *M* KMnO₄
- (c) 0.05 *M* NaOH
- (d) 0.1 *M* AgNO₃
- (e) 0.1 *M* HC₂H₃O₂

11. Calculate the molarity of the following "concentrated" reagents:

- (a) HCl specific gravity 1.19, containing 37.23 per cent by weight of HCl
- (b) HNO₃ specific gravity 1.42, containing 69.77 per cent by weight of HNO₃
- (c) H₂SO₄ specific gravity 1.84, containing 95.60 per cent by weight of H₂SO₄
- (d) NH₄OH specific gravity 0.90, containing 28.33 per cent by weight of NH₃

Ans. (a) 12.14 *M*

(b) 15.72 *M*

(c) 17.94 *M*

(d) 14.97 *M*

12. Calculate the molarity of the following solutions, the quantities given representing the grams of solute which dissolve in a liter of water:

<i>Solute</i>	<i>Grams</i>
(a) AgCl	0.0015
(b) Mg(OH) ₂	0.01
(c) MgNH ₄ PO ₄	0.1322
(d) ZnS	3.3×10
(e) CaCO ₃	0.013

13. Calculate the H⁺ ion concentration of the following series of HCl solutions:

- (a) 1.0 *M* ionized 80 per cent
- (b) 0.10 *M* ionized 92 per cent
- (c) 2.01 *M* ionized 97.2 per cent
- (d) 0.001 *M* ionized 99.0 per cent

Ans. (a) 0.80

(b) 9.2×10^{-2}

(c) 9.72×10^{-3}

(d) 9.9×10^{-4}

14. Calculate the volumes of concentrated HCl (specific gravity 1.19, containing 37.23 per cent of HCl by weight) required to make liter amounts of solutions of the following molarities:

- (a) 1 *M*
- (b) 0.1 *M*
- (c) 0.01 *M*
- (d) 0.001 *M*

15. What will be the molarity of the solution made by diluting 2.5 ml. of concentrated hydrochloric acid (specific gravity 1.19, containing 37.23 per cent by weight of HCl) in 100 ml. of water? *Ans.* 0.30 *M*

16. What is the molarity of a sulfuric acid solution made by diluting 100 ml. of concentrated reagent (specific gravity 1.84, containing 95.60 per cent of H₂SO₄ by weight) to a volume of 500 ml.?

17. A liter of $\text{HC}_2\text{H}_3\text{O}_2$ containing 0.1 gram mole of the acid is 1.34 per cent ionized. Calculate (a) the H^+ ion concentration, (b) the $\text{C}_2\text{H}_3\text{O}_2^-$ ion concentration and (c) the gram-mole concentration of non-ionized acid present.

$$\begin{aligned} \text{Ans. (a)} & 1.34 \times 10^{-3} \\ \text{(b)} & 1.34 \times 10^{-3} \\ \text{(c)} & 9.87 \times 10^{-2} \end{aligned}$$

18. Magnesia mixture contains 100.0 grams of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (as well as NH_4Cl and concentrated NH_4OH) in 1 liter of the solution. Calculate the gram-ion quantity of Mg in 1.00 ml. of this reagent, assuming that $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ is 75.0 per cent ionized in this solution.

19. What volume of a 0.1 *M* solution of HCl will be required to react with 20 ml. of a molar solution of NaOH? What volume of 0.1 *M* H_2SO_4 will be required?

$$\begin{aligned} \text{Ans. } 200 \text{ ml. of HCl} \\ 100 \text{ ml. of H}_2\text{SO}_4 \end{aligned}$$

20. Disodium phosphate reagent contains 120 grams of $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ per liter. Calculate the gram-ion quantity of PO_4 ion in 1 ml. of this reagent, assuming 75 per cent ionization.

GENERAL CONSIDERATIONS OF ANALYTICAL GROUPING

The student, in his study of general chemistry, has gained some familiarity with the structure of the atom and the arrangement of the chemical elements in the periodic table. An atom is composed, as he already knows, of a nucleus containing protons (positive charges of electricity) and neutrons, surrounded by one or more shells or orbits around which planetary electrons (negative charges of electricity) revolve. In any atom the number of planetary electrons equals the number of positive charges on the nucleus. This number is the *atomic number* of the element and differentiates one element from another.

The Periodic Table. When the elements are arranged in the order of increasing atomic numbers, periodic sequences of elements with similar chemical properties can be found in the arrangement. These similarities are shown by arranging the elements in the periodic table (page 43). Such a periodic arrangement can be strikingly correlated with the structure of the atom—in fact, the periodic table can be deduced from a study of atomic structure. In the following discussion it is assumed that the student is somewhat familiar with the periodic arrangement of the elements; a review of the subject in a textbook of general chemistry would be helpful.

Since atomic numbers range from H = 1 to U = 92, the number of planetary electrons likewise ranges between these limits. These electrons are arranged in successive groups or orbits known as

energy levels which may include a maximum of 2, 8, 18, 32, . . . electrons. It will be noted that this is the geometric series $2n^2$, $n = 1, 2, 3 \dots$. These groups are made up of subgroups, as follows: $2, 2 + 6 = 8, 2 + 6 + 10 = 18, 2 + 6 + 10 + 14 = 32$, and so on.

Starting at the beginning of the table, H has 1 electron, He has 2: With He, therefore, the first group of electrons is filled to its maximum number. To continue, Li has 2 in the first and 1 in the second group; Be has 2 and 2; B, 2 and 3; and so on; until with Ne the second group has attained its maximum number of 8 electrons. Starting with Na, electrons begin to fill in the third group until, for argon this group has reached 8 electrons.

It is possible by continuing this process and introducing additional information in some cases to derive an electronic configuration for each of the elements. Some of the more interesting of these configurations are included in the periodic table. The numbers, as written, represent the number of electrons in each electronic level in the atom. Thus, the configuration 2-8-14-2 for Fe means that there are 2 electrons in the first group, 8 in the second, 14 in the third and 2 in the fourth. In order to conserve space, if three or more orbits are filled to their maximum number, this fact is indicated by a digit in parentheses giving the number of completed orbits, followed by the number of electrons in each uncompleted orbit. Thus, for Ra, (4)-18-8-2-means that the first four groups are complete and the fifth, sixth and seventh groups contain 18, 8, and 2 electrons, respectively. The complete configuration for Ra is, then, 2-8-18-32-18-8-2.

Examination of the table reveals some striking similarities in the electronic structures of chemically similar elements. Each of the alkali metals (Li, Na, K, Rb, Cs) has a single electron in the outermost orbit; similarly, each of the alkaline earth metals (Be, Mg, Ca, Sr, Ba, Ra) has 2, and each of the halogens has 7 electrons in the outermost orbit. Moreover, it will be noticed that, for the elements appearing in the first part of the table, the number is equal to the number of the column in which the element is placed. Since, except for group VIII, this column number represents one of the common valence states of the element, the electrons in the outermost orbit in the atom sometimes are called the valence electrons.

Since atoms having the same number of valence electrons are chemically similar, it appears that these valence electrons deter-

THE PERIODIC TABLE

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TABLE I
PERIODIC CLASSIFICATION OF THE ELEMENTS

Group	I	II	III	IV	V	VI	VII	Transition Elements	VIII
Type For- mulas	$\text{R}_2\text{O}-\text{RH}$	$\text{RO}-\text{RH}_2$	$\text{R}_2\text{O}_3-\text{RH}_4$	RO_2-RH_4	$\text{R}_2\text{O}_5-\text{RH}_3$	$\text{RO}_3-\text{H}_2\text{R}$	$\text{R}_2\text{O}_7-\text{HR}$		Inert gases
Series 1	H 1.0081 1				N 14.008 2-5	O 16.0000 2-6	F 19.00 2-7		He 4.003 2
2	Li 6.940 2-1	Bc 9.02 2-2		B 10.82 2-3	C 12.00 2-4				Ne 20.183 2-8
3	Na 22.997 2-8-1	Mg 24.32 2-8-2		Al 26.97 2-8-3	Si 28.06 2-8-4	P 30.98 2-8-5	S 32.06 2-8-6	Cl 35.457 2-8-7	A 39.944 2-8-8
4	K 39.096 2-8-1	Ca 40.08 2-8-8-2		Sc 45.10 2-8-9-2	Ti 47.90 2-8-10-2	V 50.95 2-8-11-2	Cr 52.01 2-8-13-2	Mn 54.93 2-8-14-2,	Fe (55.84), 2-8-15-2, Ni (56.69) 2-8-16-2
5	Cu 63.57 (3)-1	Zn 65.38 (3)-1		Ga 69.72 (3)-3	Ge 72.60 (3)-4	As 74.91 (3)-5	Se 78.96 (3)-6	Br 79.916 (3)-7	Kr 83.7 (3)-8
6	Rb 85.48 (3)-8-1	Sr 87.63 (3)-8-2		Y 88.92 (3)-9-2	Zr 91.22 (3)-10-2	Cr 92.91 (3)-12-1	Mo 95.95 (3)-13-1	At. No. 43	Ru (101.7), Rh (102.91), Pd (106.7) (3)-15-1, (3)-16-1, (3)-18
7	Ag 107.860 (3)-18-1	Cd 112.41 (3)-18-2		In 114.76 (3)-18-3	Sn 118.70 (3)-18-4	Sb 121.76 (3)-18-5	Te 127.61 (3)-18-6	I 146.92 (3)-18-7	Xe 131.3 (3)-18-8
8	Cs 132.91 (3)-18-8-1	Ba 137.36 (3)-18-8-2		La* 158.92 (3)-18-9-2	Hf 178.6 (4)-10-2	Ta 180.88 (4)-11-2	W 183.92 (4)-12-2	Re 186.31 (4)-13-2	
9	Au 197.2 (4)-18-1	Hg 200.61 (4)-18-2		Tl 204.39 (4)-18-3	Pb 207.21 (4)-18-4	Bi 209.00 (4)-18-5	At. No. 84	Os (190.2), Ir (193.1), Pt (195.23) (4)-15-1, (4)-16-1, (4)-18	
10	At. No. 87	Pa 226.05 (4)-18-8-2		At. No. 89	Th 232.12 (4)-18-10-2	Pa 231 (4)-18-11-2	At. No. 85	Rn 222 (4)-18-8	
						U 238.07 (4)-18-12-2			

The atomic weight follows the symbol; only those elements included in the International Table are shown.
The electronic configuration is given beneath the symbol.

The elements in bold-face type are considered in the schemes of analysis.
* Fourteen other rare-earth metals occupy this same position.

mine to a very large extent the chemical behavior of the element. Each of the inert gases, except helium, contains 8 electrons in the valence orbit; no other element has such an arrangement. The presence of 8 electrons in the valence orbit makes the atom stable and chemically inactive, regardless of the maximum number that the orbit may contain. The stable group for helium is, of course, two electrons in the first orbit.

The chemical elements for whose detection provision is made in this book, a total of 32, are shown in bold-face type in the periodic table on page 43. The student will recall that, according to this periodic arrangement, the elements occupying positions toward the left of the table are the typical metals or alkali-forming elements. When their salts are dissolved in an aqueous medium they exist as positively charged ions (cations). Elements occupying the middle portions of the table are less metallic in character and may even show non-metallic properties; their salts may ionize to give both the cation and the anion form of ion: that is, they are the typical amphoteric elements. Toward the right of the table are the elements showing decidedly non-metallic properties; they form the strong acids and in the ionized form are typical anions.

The transition elements, which do not fit easily into this simple form of table and are placed between groups VII and VIII only for convenience, are typical metals.

It should be remembered that in each column or family, except for the transition elements and group VIII, there are a main group and a sub group. In this table the main group is on the left in groups I and II, with the sub group on the right; in the other columns the order is reversed. In the main groups the metallic character decreases from left to right in any row and increases from top to bottom in any family. Hence, elements such as lead and bismuth which occupy positions near the bottom of columns will have many metallic properties, whereas the elements at the top of the columns are decidedly non-metallic.

Cations. The cations, for which methods of separation and identification are given in this book, are listed here in the order in which the elements are found in the periodic groups. The cation procedure provides for the detection of 24 cations.

In periodic group I the alkali metals: sodium (Na^+); potassium (K^+); copper (Cu_2^{++} and Cu^{++}); silver (Ag^+).

In periodic group II the alkaline earth metals: magnesium (Mg^{++}); calcium (Ca^{++}); strontium (Sr^{++}); barium (Ba^{++}).

Zinc (Zn^{++}); cadmium (Cd^{++}); mercury in mercurous compounds (Hg_2^{++}) and in mercuric compounds (Hg^{++}).

In periodic group III aluminum (Al^{+++}).

In periodic group IV lead (Pb^{++}); tin in stannous compounds (Sn^{++}) and in stannic compounds (Sn^{++++}).

In periodic group V arsenic in arsenious compounds AsO_2^- , and in arsenic compounds $AsO_4^{=}$; antimony (Sb^{+++} , Sb^{+5}); bismuth (Bi^{+++}). Nitrogen in the form of the ammonium radical (NH_4^+).

In periodic group VI chromium in chromic compounds (Cr^{+++}).

In periodic group VII manganese in manganous compounds (Mn^{++}).

In the transition group iron in ferrous compounds (Fe^{++}) and in ferric compounds (Fe^{+++}); nickel (Ni^{++}); cobalt (Co^{++}).

Anions. The elements studied under the reactions of the anions are:

The halogens: fluorine, chlorine, bromine and iodine in fluorides (F^-); chlorides (Cl^-); bromides (Br^-) and iodides (I^-). Sulfur: as sulfides, ($S^{=}$); sulfites ($SO_3^{=}$); thiosulfates ($S_2O_3^{=}$) and sulfates ($SO_4^{=}$).

Chromium in chromates ($CrO_4^{=}$) and in dichromates ($Cr_2O_7^{=}$).

Nitrogen in nitrites (NO_2^-) and in nitrates (NO_3^-).

Phosphorus in phosphates ($PO_4^{=}$).

Arsenic in arsenites (AsO_2^- or $AsO_3^{=}$) and in arsenates ($AsO_4^{=}$).

Carbon in carbonates ($CO_3^{=}$) and in certain organic radicals, namely, oxalates ($C_2O_4^{=}$); acetates ($C_2H_3O_2^-$) and tartrates ($C_4H_4O_6^{=}$).

Silicon in silicates ($SiO_3^{=}$).

Boron ($B_4O_7^{=}$, BO_2^- , $BO_3^{=}$).

To this list are added the cyanogen radicals: thiocyanates (CNS^-); ferricyanides ($Fe(CN)_6^{=}$); ferrocyanides ($Fe(CN)_6^{==}$) and cyanides (CN^-).

THE ANALYTICAL GROUPING OF THE CATIONS

In the analysis of substances of unknown composition the cations are detected separately from the anions. That is, one portion of the sample is utilized for the cation analysis and another portion for the anion analysis. As already remarked, although individual reagents which yield specific tests for certain cations have been discovered, the methods of cation analysis are based on the separation of the cations into groups and subgroups. This grouping

follows, in general, the conventional macro schemes. The division of the cations into five analytical groups, through the use of the several group reagents, is based on the following behavior.

1. If a few drops of hydrochloric acid are added to a mixture containing all of the cations, precipitates of silver chloride (AgCl), mercurous chloride (Hg_2Cl_2) and lead chloride (PbCl_2) will form. Centrifuging or filtering off these chlorides will separate the silver, the mercurous mercury and most of the lead from the remaining cations. Ag^+ , Hg_2^{++} and Pb^{++} make up group I, known as the hydrochloric acid group or the silver group.

2. If the solution from which AgCl , Hg_2Cl_2 and PbCl_2 have been removed is first neutralized, then made just acid toward methyl orange test paper, and finally saturated with hydrogen sulfide, H_2S , the metallic ions, Hg^{++} , Pb^{++} , Bi^{+++} , Cu^{++} , Cd^{++} , and those of arsenic, antimony and tin will be precipitated as sulfides, having the following formulas: HgS , PbS , Bi_2S_3 , CuS , CdS , As_2S_3 , and As_2S_5 , Sb_2S_3 and Sb_2S_5 , SnS and SnS_2 . The sulfides of the other cations remaining in solution cannot form in such an acidified medium. This procedure therefore enables us to remove the afore-named metals from the remaining cations. Group II then is known as the hydrogen sulfide group or the copper-tin group. It should be noted that lead is included here as well as in group I, since the detection of lead in group I may fail.

3. If the solution which remains is treated with a small quantity of NH_4Cl to prevent the precipitation of $\text{Mg}(\text{OH})_2$, and then an excess of NH_4OH is added, the hydroxides of iron, manganese, aluminum and chromium are precipitated as $\text{Fe}(\text{OH})_3$ or $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$, $\text{Mn}(\text{OH})_2$, $\text{Al}(\text{OH})_3$ or $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ and $\text{Cr}(\text{OH})_3$ or $\text{Cr}_2\text{O}_3 \cdot x\text{H}_2\text{O}$; nickel, cobalt and zinc are transformed into complex metal-ammonia ions, that is, metal ammines. After removal of the hydroxides, the passage of a stream of H_2S into the solution will precipitate NiS , CoS and ZnS . The four hydroxides are designated as group III, subdivision A, and the sulfides as group III, subdivision B. The group as a whole is referred to hereafter as the ammonium hydroxide and ammonium sulfide group.

4. Finally, if to the remaining filtrate we add a solution of ammonium carbonate, $(\text{NH}_4)_2\text{CO}_3$, the carbonates of barium, strontium and calcium form. These constitute group IV, the ammonium carbonate or alkaline earth group.

5. Magnesium, potassium, sodium and the ammonium ion remain. There is no group precipitating agent for these, and they

are tested for separately. This is group V, the soluble cation group.

TABLE II

DIAGRAMMATIC GROUPING OF THE CATIONS

Solution	Precipitate
Ag^+	AgCl (white)
Hg_2^{++}	Hg_2Cl_2 (white)
Pb^{++}	PbCl_2 (white)
	Group I—the hydrochloric acid group
Solution	Precipitate
Hg^{++}	Hg^{++}
$[\text{Pb}^{++}]$	Pb^{++}
Bi^{+++}	Bi^{+++}
Cu^{++}	Cu^{++}
Cd^{++}	Cd^{++}
As^{+++}	As^{+++}
As^{+5}	As^{+5}
Sb^{+++}	Sb^{+++}
Sb^{+5}	Sb^{+5}
$[\text{Sn}^{++}]$	$[\text{Sn}^{++}]$
Sn^{++++}	Sn^{++++}
	Group II—the hydrogen sulfide group
Dilute HCl	Solution
Fe^{++}	Fe^{++}
Fe^{+++}	Fe^{+++}
Mn^{++}	Mn^{++}
Al^{+++}	Al^{+++}
Cr^{++}	Cr^{++}
Ni^{++}	Ni^{++}
Co^{++}	Co^{++}
Zn^{++}	Zn^{++}
	Add Br_2
Ba^{++}	Ba^{++}
Sr^{++}	Sr^{++}
Ca^{++}	Ca^{++}
	NH_4Cl
	NH_4OH
	CaCO_3
	Add $(\text{NH}_4)_2\text{CO}_3$
Mg^{++}	Mg^{++}
K^+	K^+
Na^+	Na^+
NH_4^+	NH_4^+
	Ba^{++}
	Sr^{++}
	Ca^{++}
	Mg^{++}
	K^+
	Na^+
	NH_4^+
	Solution
	Precipitate
	Fe(OH)_3 (red-brown)
	MnO(OH)_2 (brown)
	Al(OH)_3 (white)
	Cr(OH)_3 (green)
	$\text{Ni}(\text{NH}_3)_4^{++}$
	$\text{Co}(\text{NH}_3)_6^{+++}$
	$\text{Zn}(\text{NH}_3)_4^{++}$
	Pass NIS
	in CoS
	in ZnS
	Group III A—the ammonium hydroxide and sulfide group
	Group III B
	Precipitate
	BaCO_3
	SrCO_3
	CaCO_3
	Group IV—the ammonium carbonate group
	Solution
	Precipitate
	Mg^{++}
	K^+
	Na^+
	NH_4^+
	Group V—the soluble cation group

THE ALKALI METALS: SODIUM (Na^+), POTASSIUM (K^+), AMMONIUM ION (NH_4^+)

Sodium and potassium, along with lithium, cesium and rubidium, belong to the family of alkali metals. All are monovalent and fall in group I of the periodic table. They form soluble hydroxides which are strongly ionized and hence render their solutions strongly alkaline. Acidic forms of these elements do not exist; that is, they do not form amphoteric compounds; neither do they form complex ions, nor can they be oxidized to other ionic forms. All of the

common salts of sodium and potassium, and ammonium as well, are very soluble in water; they are precipitated only by reactions with the less common reagents. Because the properties of these ions are relatively so simple, they are taken up first.

The ammonium ion, though not obviously an alkali metal, is included here for study and experimentation, because in its precipitation reactions it behaves very much like potassium.

In the analytical scheme of separation followed in this book, these three ions, together with magnesium, constitute group V, the soluble cation group.

SODIUM, Na^+

The element sodium occurs widely distributed in nature, chiefly in the form of brines and rock salt. All of the common salts of sodium are very soluble in water, and some are of considerable technical importance. Metallic sodium and NaOH are prepared by the electrolytic process; the carbonate, Na_2CO_3 , and the bicarbonate, NaHCO_3 , are produced commercially by the well-known Solvay process. The carbonate, known technically as soda ash, is used in vast quantities in industries as a neutralizing agent and in certain other processes such as glass making.

When metallic sodium reacts with water according to the equation,



the strongly ionized hydroxide forms, with the liberation of hydrogen. Sodium hydroxide (caustic soda) is an important industrial chemical as well as a widely used laboratory reagent.

The triple salt which forms with zinc uranyl acetate is the best precipitation test for sodium. Zinc uranyl acetate forms a pale yellow precipitate with the sodium ion. The precipitate is hydrated sodium zinc uranyl acetate and has the composition: $\text{NaC}_2\text{H}_3\text{O}_2 \cdot \text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 6\text{H}_2\text{O}$. High concentrations of potassium will produce a similar triple salt. The reagent is a mixture of zinc acetate and uranyl acetate in dilute acetic acid solution. Nickel or magnesium uranyl acetate sometimes are employed in place of the zinc reagent.

Fluosilicic acid, H_2SiF_6 , will precipitate from solutions of sodium salts, in the presence of alcohol, a white gelatinous precipitate of sodium fluosilicate, Na_2SiF_6 . When this is used as a test for sodium, potassium must be absent, because a similar salt, K_2SiF_6 , is precipitated; the NH_4^+ ion also must be absent, because in the

presence of ammonium salts the reagent decomposes into orthosilicic acid, H₄SiO₄, which resembles Na₂SiF₆ in appearance. The reagent is not very satisfactory as a test for sodium.

Potassium pyroantimonate, K₂H₂Sb₂O₇, reacts with sodium salts in neutral or weakly alkaline solutions to precipitate sodium pyroantimonate, Na₂H₂Sb₂O₇. As a test for sodium, this reaction is not very good.

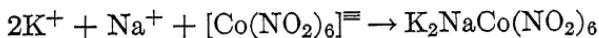
The flame test for sodium is very pronounced and sensitive, in fact so much so that it is somewhat difficult to distinguish appreciable amounts of sodium present in a sample from traces of sodium with which most reagents and materials are contaminated. The flame is an intense persistent yellow.

POTASSIUM, K⁺

This alkali metal is not nearly so abundant in nature as is sodium. The largest mineral deposit occurs in Stassfurt, Germany, where the element is found in association with magnesium chiefly in the mineral carnallite, MgCl₂·KCl·6H₂O. California saline deposits yield considerable quantities of potassium compounds. Potassium is one of the elements vital to plant growth; hence it is an important constituent in soils and fertilizers.

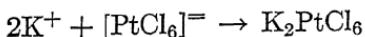
The potassium ion is monovalent. The oxide, K₂O, is relatively unimportant, but the hydroxide, KOH, is an important reagent. It is formed, like NaOH, when the metal reacts with water. A solution of KOH is highly ionized and hence strongly alkaline. The commoner salts of potassium are rather soluble in water. The insoluble salts of potassium are the cobaltinitrite, the chloroplatinate, the acid tartrate and the perchlorate. The precipitation of these salts may be used as tests for potassium, provided the ammonium ion is absent.

When sodium cobaltinitrite is added to a dilute solution containing potassium ion, there is formed a yellow precipitate of potassium sodium cobaltinitrite, according to the equation:



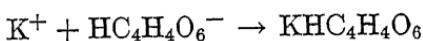
If much potassium is present, the compound will have the composition represented by the formula K₃Co(NO₂)₆. The ammonium ion precipitates (NH₄)₂NaCo(NO₂)₆, similar in appearance to the potassium compound; hence, when this reaction is used as a test for potassium, ammonium salts must be absent.

Potassium chloroplatinate, K_2PtCl_6 , a yellow precipitate, is formed when chloroplatinic acid (a solution of platinum in aqua regia) is added to a solution of a potassium salt such as the nitrate. The reaction is



This is another good test for potassium and is the basis of one of the methods for the quantitative determination of potassium. Since the NH_4^+ ion produces $(NH_4)_2PtCl_6$, similar in color, this test can only be used in the absence of ammonium salts.

A solution of tartaric acid or of sodium acid tartrate will precipitate potassium acid tartrate, $KHC_4H_4O_6$, from a neutral solution of a potassium salt:



As with the other two reactions cited, the presence of NH_4^+ interferes.

Perchloric acid, $HClO_4$, precipitates $KClO_4$ from alcoholic solutions containing K^+ ion. The reaction may be used quantitatively for the determination of potassium.

The flame test is characteristic and generally employed for the detection of potassium. The flame spectrum of potassium consists of two strong red lines (7665 and 7699 Å.) and two weaker violet lines (4044 and 4047 Å.). The flame produced by volatilizing potassium salts in the Bunsen burner flame generally is viewed through a blue glass which filters out other colors, especially the yellow of sodium. If the flame is observed through a blue "cobalt" glass, which has been spectrographically tested to have the proper qualities to transmit the red color of potassium, there will be observed a bright red flame surrounded by a blue envelope [see C. E. White, *J. Chem. Education*, **21**, 501 (1944)]. The appearance of a violet or lavender color, with or without the blue glass, is unreliable as a test for potassium.

AMMONIUM ION, NH_4^+

Ammonia, NH_3 , constitutes the starting point for the preparation of ammonium salts, which in turn furnish the ammonium ion. Most of the ammonia in commerce today is made catalytically by uniting atmospheric nitrogen with hydrogen. Ammonium hydroxide results when ammonia reacts with water. The concentrated

reagent furnished to the laboratory contains a very small amount of NH₄OH, and larger amounts of dissolved NH₃; the two solutes, when computed in terms of NH₃, represent 28.33 per cent by weight of the aqueous mixture.

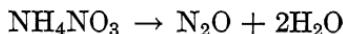
Nearly all ammonium salts are soluble to a considerable extent in water, closely resembling in this respect the salts of potassium.

Sodium cobaltinitrite, Na₃Co(NO₂)₆, gives with ammonium salts a yellow precipitate of (NH₄)₂NaCo(NO₂)₆, similar in appearance to that formed by potassium salts.

Chloroplatinic acid, H₂PtCl₆, yields a yellow precipitate of ammonium chloroplatinate, (NH₄)₂PtCl₆, with solutions containing NH₄⁺ ion. In the absence of potassium, which yields a similar precipitate, this reaction is a good test for ammonium salts and constitutes a quantitative method of analysis as well.

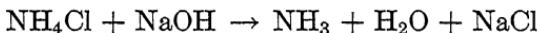
Tartaric acid, H₂C₄H₄O₆, precipitates from concentrated solutions of ammonium salts, white crystalline ammonium acid tartrate, NH₄HC₄H₄O₆, similar in appearance to the corresponding potassium compound.

Ammonium salts, as a rule, are decomposed by heating at temperatures below which the corresponding salts of sodium and potassium are volatilized. When ammonium nitrate is strongly heated, it is decomposed into nitrous oxide and water and thereby completely volatilized:



This is the basis of the method by which ammonium salts are removed from mixtures which are to be examined for potassium.

The test most commonly used to detect ammonium salts depends on the properties of ammonium hydroxide and consists in liberating NH₃ from the test mixture. If a solution containing ammonium salts is treated with a strong alkali such as NaOH, ammonia is displaced according to the reaction,



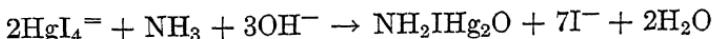
and evolved as a gas. If this is allowed to come into contact with moisture, the hydroxide is formed:



If a strip of moistened red or neutral litmus paper is held in the escaping gas, the test paper will turn blue, showing the presence of hydroxyl ions produced from the dissociation of the hydroxide

The complete explanation of the theory of this test is deferred until further in the book (see page 167).

The so-called Nessler test is very sensitive. Nessler's reagent consists of a solution of HgCl_2 in KI. These two salts react to produce the mercuric tetraiodide ion, HgI_4^- . In an excess of KOH this reagent reacts with NH_3 to produce a brown precipitate of the composition shown in the equation:



This extremely delicate test is conducted by dipping a strip of filter paper in Nessler's reagent and holding it in the gas escaping from the solution, as in the litmus-paper test. Since NH_3 is almost always present in the laboratory air, a blank test should always be run at the same time.

PRELIMINARY EXPERIMENTS

1. Zinc Uranyl Acetate Test for Sodium. To a drop of sodium test solution in a centrifuge tube add 8 drops of zinc uranyl acetate reagent. Observe the formation of the lemon-yellow precipitate, wait for a minute or two, and then centrifuge, if necessary. Write the equation for the reaction by which the precipitate is formed.

2. Flame Test for Sodium. Seal the platinum wire to be found among your equipment into a 6-inch length of glass tubing, if this has not been done already. Clean the wire thoroughly by alternately dipping it in concentrated HCl and then touching it to the upper hotter part of the flame of a Bunsen burner; do this repeatedly until color no longer is produced. Make a loop in the wire, gather up a drop of sodium test solution or a bit of a solid sodium compound, and observe the color of the flame produced when the salt is volatilized; try several different salts of sodium. Compare the color with that produced by ammonium compounds. Note that appreciable amounts of sodium give an intense persistent dandelion-yellow flame, whereas the traces of sodium present in ammonium salts and most other reagents give only a feeble dull yellow flame of short duration.

3. Precipitation Tests for Potassium. (a) *Cobaltinitrite Test.* Place a drop of KNO_3 test solution on a glass slide, and add a small amount of finely powdered sodium cobaltinitrite, $\text{Na}_3\text{Co}(\text{NO}_2)_6$. The precipitate is $\text{K}_2\text{NaCo}(\text{NO}_2)_6$. Write the ionic equation for this reaction. The ammonium ion gives a similar yellow precipitate. The test may be made more sensitive by adding a drop of AgNO_3 solution to the test solution before adding the reagent, in which case the yellow precipitate has the constitution $\text{K}_2\text{AgCo}(\text{NO}_2)_6$.

(b) *Chloroplatinate Test.* To a drop of the test solution add a drop of ethyl alcohol and then a drop of chloroplatinic acid, H_2PtCl_6 . Give the ionic equation for the reaction. Since $(\text{NH}_4)_2\text{PtCl}_6$ resembles this precipitate very closely, the test is not specific unless used in the absence of ammonium salts.

In a systematic analysis, however, ammonium salts are removed by volatilization before this test is applied.

(c) *Perchloric Acid Test.* Add to 2 drops of the test solution an equal volume of ethyl alcohol, and then add, dropwise, a dilute solution of perchloric acid, HClO_4 . The quantitative determination of potassium can be carried out by this reaction.

(d) *Precipitation of Potassium Acid Tartrate.* Add a few drops of tartaric acid solution, $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$, or sodium acid tartrate, $\text{NaHC}_4\text{H}_4\text{O}_6$, to 2 drops of test solution and shake vigorously. What is the composition of the precipitate formed?

4. Flame Test for Potassium. Clean the platinum wire, form the end into a loop, dip the wire into KNO_3 test solution contained in a watch glass and hold the wire in the upper part of a Bunsen flame. Note the color of the flame. Then observe the flame through a plate of blue glass.

Add some NaNO_3 to the KNO_3 in the watch glass, and repeat the experiment, observing the flame first without the blue glass plate and then through it. The blue glass absorbs the yellow rays produced by sodium. Describe the appearance of the flame as observed through the glass.

5. Test for the Ammonium Ion. The test for the presence of ammonium salts depends, as already stated, upon the displacement of NH_3 by treatment of the solution with NaOH . The test therefore resolves itself into showing the presence of NH_3 in the evolved gas. Place 5 drops of NH_4NO_3 test solution in a small beaker, cover with a watch glass, to the bottom of which is attached a piece of moistened red or neutral litmus paper, add 5 drops of 4 M NaOH solution, warm, and observe the result. Write the equations for the reactions involved in this test.

6. Practice Analysis of a Mixture Consisting of Ammonium, Potassium and Sodium Salts. For this first practice analysis there will be provided a mixture prepared by grinding together approximately equal amounts of NH_4NO_3 , KNO_3 and NaNO_3 . The identification of these three ions is made on portions of this sample according to the following procedure. See if you can verify the presence of each ion in the mixture.

Dissolve in a small beaker a small portion of sample in 1 ml. of water. Make the solution strongly alkaline with NaOH . Moisten a piece of red or neutral litmus paper, attach this to the bottom, convex, of a watch glass, place this over the beaker, and gently warm the bottom of the beaker. Be careful that no NaOH comes into contact with the test paper. Do not place your face over the uncovered beaker while the heating is in progress. Ammonia fumes evolved from the solution should color the paper blue. The odor of ammonia probably will be recognized.

To remove the ammonium ion so that precipitation tests can be made for potassium, place another small portion of the sample in a crucible, add 10 drops of water and heat carefully until fumes are no longer given off. Cool the crucible, test a portion of the residue for ammonia, and if it is still present, heat longer. After the crucible has cooled, add 3 or 4 drops of water and stir with the platinum wire. Warm if the residue does not dissolve. Use this solution, now free from ammonium salts, for precipitation tests for potassium and sodium.

Place a drop of the solution on a watch glass and add a bit of powdered $\text{Na}_3\text{Co}(\text{NO}_2)_6$. A yellow precipitate shows the presence of potassium.

Add 8 drops of zinc uranyl acetate solution to another drop of the solution in a centrifuge test tube. A pale yellow precipitate which develops slowly shows that sodium is present. Centrifuge if the amount of precipitate is small in order to observe it better.

Carry out flame tests on the remainder of the sample. A persistent intense yellow flame confirms the presence of sodium. Observe the flame through the blue glass plate; a red flame enveloped in blue confirms the presence of potassium.

An unknown sample containing one or more of these ions might well be issued at this time. The sample may be either a "practice" unknown, for which no grade will be recorded, or else a regular unknown, the results of which will be graded. The procedure just given should be followed. For the analysis of "unknown" samples of group V proper, which includes magnesium, the procedure on page 87 should be followed.

REVIEW EXERCISES. THE ALKALI METALS

1. Give the formula of the precipitate formed in the triple acetate test for sodium. What are the limitations of the flame test for sodium?
2. Write ionic equations for the reactions for four precipitation tests for potassium. Can these tests be conducted in the presence of sodium ion? Ammonium ion?
3. Write the series of equations involved in the evolution test for the ammonium ion.
4. Describe the flame test for potassium and the manner of conducting it.
5. Provide a scheme of analysis by which sodium, potassium and ammonium can be identified in the same sample.

CHAPTER III

THE LAW OF CHEMICAL EQUILIBRIUM. THE THEORY OF PRECIPITATION: THE SOLUBILITY-PRODUCT PRINCIPLE. THE ALKALINE EARTH ELEMENTS

The alkaline earth elements, barium, strontium and calcium, along with magnesium, are very much alike in their general properties and behavior. Their chief characteristics are their ability to form precipitates such as the carbonate, sulfate, oxalate, chromate, and their inability to undergo oxidation or to form acidic or complex ions. Accordingly their properties are relatively simple and are limited to precipitation reactions. For this reason they are introduced for study at this time. Here then we have simple examples of precipitation reactions and an excellent opportunity to introduce the law of chemical equilibrium and its application to the formation of precipitates.

THE LAW OF CHEMICAL EQUILIBRIUM

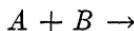
Reaction Velocity. The speed with which chemical changes takes place varies widely for different reacting substances. Thus the rusting of iron at ordinary temperatures is a comparatively slow reaction, but many other reactions take place practically instantaneously. By reaction velocity is meant the amount of reactant transformed in unit time. Reaction velocities can be measured experimentally by determining the amount of substance which is used up or formed during definite intervals of time under definite specified conditions. For the same reacting substances the velocity of reaction depends upon such factors as temperature, pressure and amount of substance present. Increase of temperature speeds up all reactions, the velocity being about doubled for every 10° C. rise in temperature. The influence of changes in temperature and pressure on a reacting system which has come to equilibrium are discussed later.

The amount of substance present and capable of reacting is a very important factor influencing the rate of reaction. The effect

of the concentration of the reacting components on the speed of the reaction, called *mass action*, is of fundamental importance in the study of chemical changes.

Mass Action. The substances undergoing change in a reaction are known as the *active masses* or the concentrations, the actual quantity being expressed in gram moles or gram ions per liter. The amount of substance transformed in unit time depends upon the amount of each reactant present, temperature and other factors remaining constant. Doubling the amount of one reactant necessarily will result in more being transformed into the products of the reaction. The effect of the mass on the reaction velocity is known as *mass action* and the generalization, which follows from this, can be stated thus: *The velocity of a reaction is proportional to the active masses present at any instant.*

Consider two substances, *A* and *B*, reacting in the proportions of one molecule or ion of *A* to one molecule or ion of *B*, according to the manner:

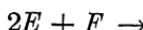


If both substances are present at the outset in equal amount, that is, in equal molar or gram-ion concentration, they will react at a certain definite rate. But the concentrations are not necessarily the same; in fact, they rarely are. The rule states that the rate at which *A* will react with *B* is proportional to the total concentrations of both *A* and *B* which are present at any instant during the reaction. The reaction velocity, that is, the rate at which the reaction takes place, will be equal to the product of the molar concentrations of *A* and *B* times a proportionality factor, *k* (a velocity constant), characteristic of this particular reaction. Algebraically this can be represented thus,

Reaction velocity = Molar conc. of *A* \times molar conc. of *B* \times *k*
or more simply, if we let *C* stand for the molar concentration of any particular reacting component and *v* for the reaction velocity:

$$v = C_A \times C_B \times k$$

If in some other reaction, for example, between the substance *E* and *F*, in which two molecules or ions of *E* react with one of *F* as in the manner,



the reaction rate is dependent upon the simultaneous collisions.

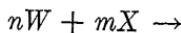
of two particles of E with one of F . In this case the reaction-velocity equation takes the form,

$$v = C_E \times C_E \times C_F \times k'$$

or, if the factor, C_E , representing to total concentration of E is squared:

$$v = (C_E)^2 \times C_F \times k'$$

In general, in a reaction in which n molecules or ions of one substance, W , react with m molecules or ions of another substance, X , according to the manner,



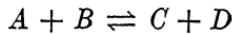
the generalized velocity equation becomes

$$v = (C_W)^n \times (C_X)^m X k''$$

the total molar concentration of each reactant being raised to a power equal to the coefficient representing the number of like reacting molecules or ions.

Reversibility of Reactions. The extent to which a reaction will proceed in one direction depends, among other factors, upon the nature of the products formed. If the newly formed products show any tendency of interacting among themselves to reform the initial reactants, an opposing action will be set up in the reverse direction, and the net effect will be that the entire amounts of the initial components are not transformed when the reaction appears to stop. Some reactions show a marked tendency to reverse, so much so that they are of little value in analytical chemistry. In other reactions, reversibility is less pronounced, and here the reactions run nearly, but *not entirely*, to completion. These are the analytically useful ones as will be emphasized later. *All reactions are reversible to a certain extent.* This point cannot be overemphasized, because it is the basis upon which the fundamental theory rests.

Equilibrium. In all reacting systems, therefore, a condition will be reached where a certain, even though small, concentration of the initial reactants can exist side by side with the products of the reaction, apparently without further change taking place. A state of dynamic equilibrium is set up, equilibrium, which means that for a reversible reaction such as



when equilibrium has been reached, the reactants A and B are reacting to form C and D at exactly the same rate that C and D are reacting to form A and B . Equilibria are set up in all sorts of reacting systems: for example, between gases, between dissolved molecules and their ions, between precipitates and the solution that surrounds them and between substances distributed between two solvents. The fundamental law which expresses the state of equilibrium is called the Law of Chemical Equilibrium and is of extreme importance in the study of reactions. The theory of reactions is based on this law, and it is the most fundamental principle with which we have to deal.

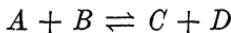
The Law of Chemical Equilibrium. In considering the reaction between A and B , we derived the algebraic expression for the reaction velocity, namely,

$$v_1 = C_A \times C_B \times k_1 \quad (1)$$

where C stands for the molar concentrations and k_1 is a velocity constant characteristic of the reaction between A and B . Suppose we apply a similar equation to another set of reacting substances, say to C and D . This will be characterized by a different velocity, v_2 , and a different velocity constant, k_2 :

$$v_2 = C_C \times C_D \times k_2 \quad (2)$$

Now suppose that the substances C and D are the products resulting from A and B and, vice versa, A and B are the products resulting from C and D as in the reversible reaction:



Hence C and D are forming during the reaction at a rate dependent upon the amounts of A and B present. As A and B are used up, their masses decrease and the reaction velocity in the direction of C and D decreases. But the amounts of C and D are increasing continually and will interact to reform A and B . When the amounts of C and D are in such proportions as to cause the reaction to reverse at the same rate that it is proceeding forward, a dynamic state of equilibrium is set up, as previously indicated. The velocities are then equal in both directions. We then can apply the velocity equations to a reaction going in both directions, at the point where the concentrations are in such proportions as to make the velocity forward equal to the velocity backward. If the two

algebraic equations which express the relation between velocity and concentration are equated, we have

$$v_1 = C_A \times C_B \times k_1 = v_2 = C_C \times C_D \times k_2$$

Therefore,

$$C_A \times C_B \times k_1 = C_C \times C_D \times k_2$$

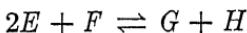
If we divide by $C_A \times C_B$ and transfer k_2 , the equilibrium ratio is obtained:

$$\frac{C_C \times C_D}{C_A \times C_B} = \frac{k_1}{k_2}$$

The ratio of the products of the molar concentrations is then equal to the ratio of the velocity constants, when equilibrium is reached. The ratio k_1/k_2 can be designated K , and then becomes an equilibrium constant characteristic of this reaction. The equilibrium expression then is written:

$$\frac{C_C \times C_D}{C_A \times C_B} = K \quad (\text{equilibrium constant})$$

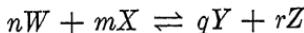
In a reaction such as



where two molecules of E react with one of F , the total concentration of E is squared and the equilibrium formula becomes

$$\frac{C_G \times C_H}{(C_E)^2 \times C_F} = K$$

For the most general case, for a reaction of the type,

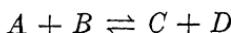


the most generalized equilibrium expression is

$$\frac{(C_Y)^q \times (C_Z)^r}{(C_W)^n \times (C_X)^m} = K$$

The Law of Chemical Equilibrium states that: *In a reacting system, when equilibrium is reached, the product of the molar concentrations of the products of the reaction divided by the product of the molar concentrations of the reactants (each concentration raised to a power equal to the coefficient representing the number of like reacting parts which enter into the reaction) is always equal to a constant.*

The algebraic expression will take on modified forms in the several applications which follow. For each reaction for which the law strictly holds, at constant temperature and pressure, the numerical value of the equilibrium constant is always the same. No matter how much the concentration of any one component in the reaction mixture varies, the proportions of the other components must change until equilibrium is again established and the value of K restored. Thus if the amount of A is increased in the reversible reaction,



the reaction will run faster in the direction of the formation of C and D , more of these products will be formed, reaction will reverse at a faster rate than originally, and again equilibrium will be established, with the proportions A , D , C and D changed but the ratio of the products of their molar concentrations still the same.

If the pressure on a system in equilibrium is increased, there will be a change in the proportions of the reacting components when the new equilibrium is established at the higher pressure. Of the two opposing reactions, that one will be favored which leads to a reduction in the volume of the system. This is particularly significant in gaseous reactions. There is thus a shift or displacement in the equilibrium concentrations, the system again coming to equilibrium with different proportions of the reacting components. A change of pressure, however, does not change the value of the equilibrium constant.

When the temperature of a reacting system in equilibrium is changed, there is a change in the value of the equilibrium constant; that is, a new ratio is established for the equilibrium concentrations at the new temperature. With a rise in temperature, the equilibrium is shifted in the direction favoring the reaction which absorbs heat. The system as a whole tends to oppose the effect of the added stress placed on it; it does this by favoring that reaction which uses up the heat supplied in raising the temperature.

The effect of changes in concentration, pressure and temperature on a system in equilibrium is summed up in a very general law known as Le Chatelier's Law, which states: *Whenever a stress is applied to a system in equilibrium, that reaction will be favored which tends to offset or annul the effect of the stress.* Thus, increasing the concentration of one reactant causes the reaction to proceed faster in order to lower this concentration. Increased pressure will be

opposed by that reaction which tends to relieve the pressure by reducing the volume. Raising the temperature favors the reaction, which, by absorbing heat, tends to lower the temperature.

The Law of Chemical Equilibrium is of wide application to a great variety of reactions. It was first shown to hold for reactions between molecules of organic substances. It is applied also to molecular gas reactions. In the reactions of qualitative analysis a number of important ionic equilibria are encountered. These equilibria are discussed in the following sections. They will be taken up in this order:

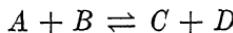
1. Equilibria of ions of precipitates (solubility-product constants).
2. Amphoteric equilibria.
3. Equilibria of complex ions (instability constants).
4. Ionization equilibria (ionization constants).
5. Hydrolysis equilibria (hydrolysis constants).
6. Oxidation-reduction (*redox*) equilibria.

THE THEORY OF PRECIPITATION: THE SOLUBILITY-PRODUCT PRINCIPLE

The equilibrium conditions existing in solutions in which precipitates are being formed or are being dissolved are extremely important, because practically all of the separations and many of the final tests in qualitative analysis involve either the formation or the dissolving of precipitates. It is therefore of considerable importance to know the conditions under which a precipitate is formed and what ionic changes take place when a precipitate dissolves. This application of the Law of Chemical Equilibrium is known as the solubility-product principle. In the following paragraphs are shown how the special equilibrium constants, which characterize the equilibria in such solutions, are calculated and how the principle is applied to the formation of precipitates.

Derivation of the Principle. Any solid substance will dissolve in a given quantity of solvent until the saturation quantity is reached. The quantity required for saturation varies over wide limits; for a sparingly soluble substance such as a precipitate formed in a reaction, saturation is soon reached. The dissolved substance, however, if it is an electrolyte, does not remain in the molecular form, but dissociates for the most part into its respective ions; in most cases the ionization can be considered complete.

The equation expressing the relationship between the concentrations of the initial and final products of a reaction such as



is given by the equation:

$$\frac{C_C \times C_D}{C_A \times C_B} = K$$

This can be transformed for the special reaction of precipitation,



into the special equilibrium equation,

$$\frac{C_{A^+} \times C_{B^-}}{C_{AB}} = K$$

where C_{AB} is the concentration of the precipitate formed.

Since, however, after equilibrium is reached in a precipitation reaction, the amount of solid precipitate present does not affect the equilibrium of the ions in the solution, the expression can be re-written simply as

$$C_{A^+} \times C_{B^-} = K_{s.p.}$$

This new constant is called the solubility-product constant. It is a special equilibrium constant, relating to the equilibrium of the ions in a saturated solution. It can be used rigorously only for solutions formed from difficultly soluble compounds. The expression means that in a solution containing ions, which by their union produce a difficultly soluble compound, the ions will be in equilibrium when the product of their gram-ion concentrations attains a certain definite small value, called the solubility-product constant. When this constant is reached, the solution is saturated with respect to the ions contained therein. The constant has a different numerical value for each slightly soluble compound and will vary with the temperature for the same compound.

For the compound E_2F , in which 2 ions of E are involved for every ion of F , in the reaction: $2E^+ + F^- \rightarrow E_2F$ the expression becomes

$$(C_{E^+})^2 \times C_{F^-} = K_{s.p.} \text{ (of } E_2F\text{)}$$

In general for the compound W_nX_m , the total concentration of W is raised to the n th power and that of X to the m th power.

If the value for the constant is exceeded, the excess ions will unite to form a solid compound, that is, a precipitate. In any solution in which there is undissolved solid, no matter how little or how much, the solution surrounding the solid always will contain enough of the ions to make the product of their gram-ion concentrations equal to the constant characteristic for that particular solid. This ion relationship as already noted holds only for relatively insoluble compounds.

Calculation of Solubility-Product Constants. Solubility-product constants have been determined for many of the compounds which are obtained as precipitates in analytical work. They generally are calculated from the solubility data. The solubility in grams per liter, determined by experiment, is converted into the molar solubility by dividing by the molecular weight of the dissolved compound. From this the concentration in gram ions per liter of each set of ions may be calculated. If it is known that the ionization of the dissolved solute is not complete, the molar solubility is multiplied by the percentage to which the solute ionizes.

Some examples will show how these constants are calculated.

Example 1. Calculate the solubility-product constant of AgCl, the solubility of AgCl in a liter of water at 25° C. being 0.0015 gram.

The molecular weight of AgCl is 143.34. Dividing 0.0015, the gram solubility, by 143.34 gives 0.0000106 gram mole; that is, a liter of AgCl solution is 0.0000106 molar with respect to the total solute. Since this is an extremely dilute solution, it is completely ionized, and the solution therefore contains 0.0000106 gram ion of Ag⁺ ion and 0.0000106 gram ion of Cl⁻ ion.

The solubility-product constant calculated from the equation,

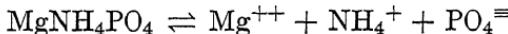
$$\begin{array}{rcl} C_{\text{Ag}^+} & \times & C_{\text{Cl}^-} \\ 0.0000106 & \times & 0.0000106 \end{array} = K_{\text{s.p.}} = 0.0000000011$$

is therefore 1.1×10^{-10} .

Where three different sets of ions are formed from a dissolved solid, the product of the gram-ion concentration of all three sets is the desired $K_{\text{s.p.}}$. The case of MgNH₄PO₄, the precipitate formed in the tests for magnesium and phosphate ions, is a good example where three different sets of ions are involved in the equilibrium.

Example 2. Calculate the $K_{\text{s.p.}}$ of MgNH₄PO₄, the solubility of which is 0.0086 gram per liter.

The ionization of this compound takes place according to the reaction,



Dividing the gram solubility, 0.0086, by 137.38, the molecular weight, gives 6.3×10^{-5} as the molar solubility. Since complete ionization is assumed, this value, 6.3×10^{-5} , is assigned to the concentration of each set of ions.

The solubility-product equation is

$$C_{\text{Mg}^{++}} \times C_{\text{NH}_4^+} \times C_{\text{PO}_4^{=}} = K_{\text{s.p.}} \text{ of } (\text{MgNH}_4\text{PO}_4)$$

By substituting the numerical values of the gram-ion concentrations of each set of ions, we obtain

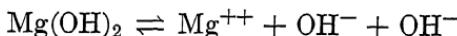
$$(6.3 \times 10^{-5}) \times (6.3 \times 10^{-5}) \times (6.3 \times 10^{-5}) = 2.5 \times 10^{-13}$$

the constant being therefore 2.5×10^{-13} .

If the dissolved solid yields 3 ions, 2 of which are alike, the total gram-ion concentration of each set of ions must be determined from the molar solubility of the dissolved solute; after this the total concentration is squared for that set which appears twice in the equation. This may be made clear in the case of Mg(OH)_2 .

Example 3. Calculate the solubility-product constant for Mg(OH)_2 .

This substance ionizes according to the equation,



and yields 1 magnesium ion and 2 hydroxyl ions for each molecule ionized. The equilibrium expression is therefore

$$C_{\text{Mg}^{++}} \times C_{\text{OH}^-} \times C_{\text{OH}^-} = K_{\text{s.p.}}$$

or

$$C_{\text{Mg}^{++}} \times (C_{\text{OH}^-})^2 = K_{\text{s.p.}}$$

The molar solubility of Mg(OH)_2 at room temperature is 0.000206; hence, the concentration of Mg^{++} ion is 0.000206 gram ion per liter, and the concentration of the hydroxyl ion is twice as great, or 0.000412 gram ion per liter. The value of the constant is therefore

$$\frac{C_{\text{Mg}^{++}}}{0.000206} \times \frac{(C_{\text{OH}^-})^2}{(0.000412)^2} = \frac{K_{\text{s.p.}} [\text{Mg(OH)}_2]}{3.5 \times 10^{-11}}$$

Solubility-product constants of a number of slightly soluble substances are given in Table XXVIII in the Appendix for which the

data were collected from various sources. Most of these results have been calculated from solubility data obtained by measuring the electric conductivity of the saturated solutions. Because of the experimental difficulties encountered in such measurements, the calculated solubility-product constants of many compounds are so uncertain as to be practically valueless. This is true especially of most hydroxides and many sulfides, and for this reason values for many of these compounds are omitted from the table. Also, different values for the same constant are given by different investigators; those included here are believed to be the most reliable.

The solubility-product constant, like the solubility, changes with the temperature. The values here given apply with reasonable accuracy to solutions at ordinary room temperatures. Room temperature is assumed in all of the following problems involving solubility-product constants.

Calculation of the Solubility and the Gram-Ion Concentration From the Solubility-Product Constant. If the $K_{s.p.}$ is known, the concentration of the ions, the molar solubility and the gram solubility may be readily found.

Example 4. What is the solubility of CaCO_3 in grams per liter, the $K_{s.p.}$ being 1.7×10^{-8} ?

This salt ionizes according to the reaction,



The solubility-product equation is

$$C_{\text{Ca}^{++}} \times C_{\text{CO}_3^-} = K_{s.p.}$$

In a saturated solution of CaCO_3 , the concentration of calcium ion will be equal to that of the carbonate ion. By letting x stand for concentration of each set of ions, we obtain

$$x \times x = 1.7 \times 10^{-8}$$

$$x^2 = 1.7 \times 10^{-8}$$

$$x = \sqrt{1.7 \times 10^{-8}}$$

$$x = 1.3 \times 10^{-4}$$

Since 1.3×10^{-4} is the gram-ion concentration of both the Ca^{++} and the CO_3^- ion, it is likewise the molar solubility of

CaCO_3 . To convert moles into grams multiply by the molecular weight. Therefore

$$1.3 \times 10^{-4} \times 100.07 = 1.3 \times 10^{-2} \text{ gram per liter}$$

Example 5. What are the gram-ion quantities of Mg^{++} ion and OH^- ion in 200 ml. of a saturated solution of $\text{Mg}(\text{OH})_2$, the $K_{\text{s.p.}}$ being 3.5×10^{-11} ?

First find the concentrations in a liter. The equation is

$$C_{\text{Mg}^{++}} \times (C_{\text{OH}^-})^2 = K_{\text{s.p.}}$$

Letting x equal the magnesium concentration and $2x$ the hydroxyl concentration, we have

$$x \times (2x)^2 = 3.5 \times 10^{-11}$$

$$4x^3 = 3.5 \times 10^{-11}$$

$$x^3 = 8.8 \times 10^{-12}$$

$$x = 2.1 \times 10^{-4}$$

Therefore $C_{\text{Mg}^{++}} = 2.1 \times 10^{-4}$ and $C_{\text{OH}^-} = 4.2 \times 10^{-4}$, the concentrations in 1000 ml. of the solution. In 200 ml. there are 200/1000 or 0.2 of the foregoing amounts.

$$C_{\text{Mg}^{++}} = 2.1 \times 10^{-4} \times 0.2 = 4.2 \times 10^{-5}$$

$$C_{\text{OH}^-} = 4.2 \times 10^{-4} \times 0.2 = 8.4 \times 10^{-5}$$

Application of the Solubility-Product Principle to Precipitation. The solubility-product constant gives a measure of the concentration of ions which are in equilibrium in a saturated solution of a sparingly soluble electrolyte. This value must be reached to establish equilibrium and must be exceeded before a solid, that is, a precipitate, will separate out. Since the constant is a product of two or more factors expressing concentration of ions in equilibrium, these concentrations need not necessarily be equal to each other, as was the case in calculating the constants from pure solutions of the compound; all that is required for equilibrium to be established is for the product of the gram-ion concentrations to reach the numerical value of the constant for the compound in question.

What happens during the formation of a precipitate is this: Precipitating ions are added, in the form of a solution of an elec-

trolyte, to the solution which contains the ions to be precipitated. When an amount of precipitating ions is added such that the product of the ion concentrations (the gram-ion concentration of precipitating ions \times gram-ion concentration of ions to be precipitated) is exactly equal to the $K_{s.p.}$, the ions will be in equilibrium and the solution will be saturated. Addition of a further amount of precipitating reagent will result in the formation of a precipitate, since the solution already is saturated with ions. The solid will continue to separate during the addition of precipitating ions, until the ions whose precipitation is desired have been practically but not entirely removed from solution. At all times after a precipitate has initially formed, the solution surrounding it contains the two or more sets of ions in such amounts that the product of their gram-ion concentrations always equals the solubility-product constant.

In applying the solubility-product principle to the formation of precipitates, under varying circumstances, there are three cases to be considered, namely:

1. The formation of a single precipitate.
2. The simultaneous precipitation of two or more similar compounds by the same precipitating reagent (This phenomenon is known as fractional precipitation; it is illustrated on page 72).
3. Controlled or buffered precipitation, discussed at length in Chapter V.

To illustrate the application of this principle let us consider a few simple cases.

Example 6. Suppose it is desired to demonstrate the presence of silver ion in a solution by the formation of AgCl through the addition of chloride ion, the solution containing 0.0001 gram ion of Ag^+ per liter. What concentration of chloride ion is required to initiate the formation of AgCl?

The solubility-product equation for AgCl is

$$C_{\text{Ag}^+} \times C_{\text{Cl}^-} = K_{s.p.}$$

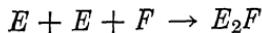
The C_{Ag^+} is 0.0001 and the $K_{s.p.}$ is 1.1×10^{-10} . Let x = the C_{Cl^-} required to establish equilibrium. By solving for x in the equation,

$$0.0001 \times x = 1.1 \times 10^{-10}$$

we find that 0.0000011 or 1.1×10^{-6} gram ion of chloride is required to saturate this solution. Any quantity, however small,

in excess of this concentration will result in the visible precipitation of AgCl , giving the desired test for silver.

Where 2 ions of one kind react with an ion of another kind as, for instance, in the precipitation of a salt of the type E_2F , the precipitation reaction is



for which the solubility-product equation is expressed by

$$(C_E)^2 \times C_F = K_{\text{s.p.}}$$

Note that in this case the total concentration of E is squared in the equilibrium formula. The following examples illustrate the calculation.

Example 7. What CrO_4^- ion concentration is necessary to produce a precipitate of Ag_2CrO_4 in a liter of solution containing 0.001 gram ion of Ag^+ ion?

Here the total Ag^+ ion concentration is given, namely, 0.001 gram ion. This concentration must be squared. By letting x equal the CrO_4^- ion concentration required to saturate the solution, we obtain

$$(C_{\text{Ag}^+})^2 \times C_{\text{CrO}_4^-} = K_{\text{s.p. of } \text{Ag}_2\text{CrO}_4}$$

$$(0.001)^2 \times x = 1.7 \times 10^{-12}$$

$$x = \frac{1.7 \times 10^{-12}}{(0.001)^2}$$

$$x = 1.7 \times 10^{-6}$$

Example 8. What hydroxyl-ion concentration is required barely to saturate a solution which contains 0.0035 gram ion of Mg^{++} per liter of solution? The $K_{\text{s.p.}}$ of $\text{Mg}(\text{OH})_2$ is 3.5×10^{-11} .

The solubility-product equation is

$$C_{\text{Mg}^{++}} \times (C_{\text{OH}^-})^2 = K_{\text{s.p.}}$$

$$3.5 \times 10^{-3} \times (x)^2 = 3.5 \times 10^{-11}$$

$$x^2 = 1 \times 10^{-8}$$

$$x = 1 \times 10^{-4}$$

Therefore 1×10^{-4} gram ion of OH^- is required to saturate the solution with respect to Mg^{++} and OH^- ; any excess over this amount results in the precipitation of $\text{Mg}(\text{OH})_2$.

The numerical value of the solubility-product constant, it must be remembered, is calculated from the concentrations in a liter of the saturated solution of the pure salt. For any other volume the product would have some other value. Thus, in the case of AgCl, since 0.0015 gram or 0.00001 gram mole of the solid dissolves in 1000 ml. of water, the gram-ion concentrations of Ag and Cl⁻ are both 1×10^{-5} . On the other hand, 100 ml. of water would dissolve only 0.00015 gram, and the quantity of Ag⁺ ion and Cl⁻ ion present in 100 ml. of the solution would be only 1×10^{-6} ; for 10 ml. the amount would be 1×10^{-7} , and for 1 ml. only 1×10^{-8} . Obviously, for each of these volumes the solutions are saturated. In calculations involving the solubility-product constant, in order to avoid confusion, it should be borne in mind that the convention is to use the value for a liter of saturated solution.

In actual practice, the volume of solution in which a precipitation test is desired is much less than 1 liter; tests usually are conducted in less than 1 ml. of solution. Since the value of the constant is based on the concentrations in 1000 ml., it is more desirable to convert the gram-ion quantities in the given test solution to the corresponding value for a liter, calculate the concentration of the precipitating ion on a liter basis, and then reconver the quantity to the given volume. This is illustrated for a simple case in example 9.

Example 9. What quantity of chloride ion is required to start the precipitation of AgCl in 5 ml. of a solution which contains 0.0001 gram ion of Ag⁺ ion? The $K_{s.p.}$ of AgCl is 1.1×10^{-10} .

Since in 5 ml. there is 0.0001 gram ion of Ag, in 1000 ml. the concentration would be $1000/5$ or 200 times 0.0001 or 0.02 or 2×10^{-2} gram ion. Therefore

$$C_{\text{Ag}^+} \times C_{\text{Cl}^-} = K_{s.p.}$$

$$2 \times 10^{-2} \times x = 1.1 \times 10^{-10}$$

$$x = 5 \times 10^{-9} \text{ gram ion of Cl}^- \text{ in 1 liter}$$

In 5 ml. the amount needed would be $(5 \times 10^{-9})/200$ or 2.5×10^{-11} gram ion.

In practical work, either the weight in grams of precipitating agent or the volume of solution of the precipitating reagent is required, rather than the amount expressed in terms of gram ions.

That is, we may wish to know the grams of precipitating reagent or the volume of reagent necessary to give the specified test.

In case the weight in grams of the precipitating ion is wanted, the calculation is made very simply by multiplying the gram-ion concentration needed for saturation, as calculated for the volume of solution in which precipitation is to take place, by the molecular or atomic weight of the ion.

If the weight of compound which furnishes the precipitating ion is wanted, multiply the gram-ion concentration needed for saturation by the molecular weight of the compound used as precipitating agent.

Example 10. What weight in grams of AgNO_3 is required to give a test for chlorides, in 10 ml. of a solution which contains 0.0001 gram ion of Cl^- ion?

The $K_{\text{s.p.}}$ of AgCl is 1.1×10^{-10} . The Cl^- ion concentration corresponding to a liter of solution is 0.0001×100 or 0.01 gram ion.

$$C_{\text{Ag}^+} \times C_{\text{Cl}^-} = 1.1 \times 10^{-10}$$

$$x \times 0.01 = 1.1 \times 10^{-10}$$

$$x = 1.1 \times 10^{-10} \text{ gram ion of } \text{Ag}^+ \text{ required for 1 liter}$$

or 1.1×10^{-10} for precipitation to start in 10 ml. The quantity of AgNO_3 needed to furnish this is 1.1×10^{-8} gram mole. The weight is therefore $1.1 \times 10^{-10} \times 169.9$ or 1.87×10^{-8} gram of AgNO_3 .

In calculating the volume of precipitating reagent required to start the precipitation, a complication arises in the computation in that the saturation concentrations are dependent upon the total volume of the mixture of test solution and reagent. However, if the concentration in the test solution is known, we can determine by calculation whether a certain volume of reagent will give a precipitate.

Example 11. If 10 ml. of AgNO_3 reagent containing 0.001 gram ion of Ag^+ ion are added to 10 ml. of test solution containing 0.001 gram ion of Cl^- ion, will a precipitate of AgCl form?

$$C_{\text{Ag}^+} \times C_{\text{Cl}^-} = 1.1 \times 10^{-10}$$

$$0.05 \times 0.05 = 0.0025$$

The product of the gram-ion concentrations, referred to a liter, greatly exceeds the $K_{\text{s.p.}}$, and AgCl therefore will be precipitated.

The use of the solubility-product principle in precipitation calculations determines the concentrations of ions which remain in the solution in equilibrium with each other. Primarily such a calculation is of value in predicting when a precipitate may form; it distinctly does not determine how much precipitate may be obtained by the use of a certain amount of reagent. The solubility-product equation, however, enables one to determine the equilibrium concentrations of ions which remain during the progress of precipitate formation. Let us apply this to the progressive precipitation of AgCl. Suppose we start with a liter of solution containing 0.1 gram ion of Ag and gradually add Cl⁻ ions. Table III shows the concentrations of Ag⁺ ion and Cl⁻ in equilibrium at the several stages of the precipitation, the concentration of the Cl⁻ ion being at each stage calculated from the equation

$$C_{\text{Ag}^+} \times C_{\text{Cl}^-} = 1.1 \times 10^{-10}$$

TABLE III

CONCENTRATION OF Ag⁺ ION AND Cl⁻ ION IN EQUILIBRIUM AT THE SEVERAL STAGES OF PRECIPITATION

<i>Stage of Precipitation</i>	C_{Ag^+}	C_{Cl^-}
Original solution	0.1	0
When first saturated	0.1	1.1×10^{-9}
When one tenth is precipitated	0.09	1.1×10^{-9}
When one half is precipitated	0.05	2.2×10^{-9}
When nine tenths are precipitated	0.01	1.1×10^{-9}
When equivalent Ag has been added	1.05×10^{-5}	1.05×10^{-5}

Fractional Precipitation. Thus far the solubility-product principle has been applied to cases in which only a single compound has been precipitated. Special cases, however, arise, as in the precipitation of groups of ions, where two or more sets of ions are present and capable of being precipitated by the same precipitating reagent. In the chlorides of cation group I, the sulfides of groups II and III, the carbonates and sulfates of group IV and the halides of silver, the precipitation of several similar salts takes place as a result of the use of a single precipitant. This phenomenon is known as fractional precipitation.

These questions naturally arise: (1) which ion will be precipitated first, and (2) will the first set of ions be completely precipitated before the other set of ions begins to be precipitated? From a consideration of the concentrations of the ions in the same solu-

tion, it follows that, when the precipitating ion is added, the solution will become saturated first with respect to that salt which has the smallest solubility product. The first precipitate formed therefore will be that of the least soluble compound. This will continue to form upon further addition of reagent until the value of the $K_{s.p.}$ of the second set (in the order of increasing solubility) is reached. At this stage, the two ions forming the two least soluble salts will be precipitated simultaneously. From this point on, the concentrations of the ions still remaining in solution will bear a direct ratio to the solubility-product constants of the two salts being precipitated.

To take a specific example, let us suppose a solution contains equal concentrations of chloride and bromide ion to which silver nitrate is slowly added. The $K_{s.p.}$ of AgBr is 3.5×10^{-13} and that of AgCl is 1.1×10^{-10} . Obviously, the solution will become saturated first with respect to AgBr , since its $K_{s.p.}$ is smaller than that of AgCl . Pure AgBr will continue to form until enough Ag^+ ion has been added to reach the $K_{s.p.}$ of AgCl . Thereafter there will be simultaneous precipitation of both AgBr and AgCl .

Example 12. What is the ratio of concentrations of Br^- ion to Cl^- ion, in a solution to which sufficient Ag^+ ion has been added to cause the precipitation of both AgBr and AgCl ?

When both salts are being formed, the desired ratio is directly equal to the ratio of the solubility-product constants; that is,

$$\frac{3.5 \times 10^{-13}}{1.1 \times 10^{-10}} = \frac{C_{\text{Br}^-}}{C_{\text{Cl}^-}} = 3.2 \times 10^{-3}$$

The ratio is 3.2×10^{-3} ; this means that the concentration of Br^- ion is 3.2×10^{-3} times that of the chloride-ion concentration when both salts are being precipitated; that is, the bromide-ion concentration is about one-thousandth that of the chloride-ion concentration.

If the concentration of that ion whose salt has the greater $K_{s.p.}$ value is in excess, the salt of this ion will be partly precipitated first. Thus in a solution which contains a large excess of Cl^- ion over that of Br^- ion, the $K_{s.p.}$ of AgCl will be the first exceeded. After the concentration of Cl^- ion thus has been lowered to such an extent that, with further addition of Ag^+ ion the $K_{s.p.}$ of AgBr is also exceeded, both salts will precipitate simultaneously.

Where three or more salts are to be precipitated, as in group precipitation, the calculations become somewhat more complicated.

Contamination of Precipitants. When any precipitate separates from a solution it carries with it from the solution, either occluded within the crystals or adsorbed on the surface, some of the cations and anions which normally constitute soluble compounds. Thus, if AgCl is precipitated from solutions of AgNO_3 and NaCl , the precipitate, even after washing, will contain some NaCl . This phenomenon is called *coprecipitation*. The soluble coprecipitated compound very frequently has one ion in common with the precipitate.

If the foreign substance is not carried down along with the main precipitate but forms later on the surface of the particles, it is said to be postprecipitated; this phenomenon is called *postprecipitation*. This effect is noticed particularly with the sulfides. Zinc, for instance, will not precipitate as ZnS , when a 0.01 *M* solution of a zinc salt, in a solution which contains 0.3 of a gram ion of hydrogen ion, is saturated with H_2S , even though the solution is supersaturated with ZnS . If, however, Hg^{++} , Cu^{++} or some other metallic ion which forms a very insoluble sulfide is present, this sulfide will precipitate immediately when H_2S is added, and ZnS then will be precipitated from the supersaturated solution onto the surface of the other sulfide. In this way as much as 95 per cent of the zinc in a solution may be postprecipitated on another sulfide under conditions such that, if the second sulfide were not present, no ZnS would appear.

In schemes of qualitative analysis which utilize H_2S to precipitate Hg^{++} , Pb^{++} , Bi^{+++} , Cu^{++} , Cd^{++} , and so forth, from acid solution, a large proportion of any Zn^{++} present may be postprecipitated on these sulfides and therefore lost. This may account for the difficulty that is sometimes experienced in detecting zinc at its proper place in the scheme of analysis.

It is to be noted that the failure of ZnS to precipitate when H_2S is passed into a moderately acid solution of a zinc salt is due, not to its solubility, but apparently to the slowness of the reaction and to the formation of a highly supersaturated solution of ZnS . The presence of other sulfides does not render the ZnS less soluble but simply promotes precipitation from an already supersaturated solution.

It must not be supposed that postprecipitation is limited to zinc sulfide or even to sulfides in general. The only requirement for postprecipitation is that the solution be supersaturated with respect to some constituent which normally would not be precipitated because of the slowness of crystallization.

Contamination is especially high for those precipitates which are obtained in a gelatinous form, such as the hydrated oxides of iron and aluminum. Much of the contamination is due to the large amount of mother liquor included in the precipitate; this can be removed by repeated washing. However, there is an appreciable amount of adsorbed contaminants which cannot be removed by washing.

QUESTIONS AND PROBLEMS—SET 3. SOLUBILITY-PRODUCT CALCULATIONS

1. Calculate the solubility-product constants of the following relatively insoluble salts, assuming complete ionization, the solubility in moles per liter being given:

Salt	Solubility, Moles per Liter	
(a) AgBr	5.9×10^{-7}	Ans. (a) 3.5×10^{-13}
(b) CaCO ₃	1.3×10^{-4}	(b) 1.7×10^{-8}
(c) BaSO ₄	1.1×10^{-5}	(c) 1.2×10^{-10}

2. Calculate the solubility-product constants of the following salts, assuming complete ionizations:

Salt	Solubility, Moles per Liter
(a) MnS	3.8×10^{-8}
(b) HgS	6.3×10^{-27}
(c) AgBr	5.9×10^{-7}

3. Calculate the solubility-product constants of the following salts, given the solubility in grams per liter, and assuming complete ionization:

Salt	Solubility, Grams per Liter	
(a) PbBr ₂	9.7×10^{-4}	Ans. (a) 3.4×10^{-5}
(b) Pb ₃ (PO ₄) ₂	1.7×10^{-4}	(b) 2.5×10^{-18}
(c) K ₂ PtCl ₆	11.0×10^{-4}	(c) 4.9×10^{-5}

4. Calculate the solubility-product constants of the following relatively insoluble salts, assuming complete ionization, the solubility in grams per liter being given:

Salt	Solubility, Grams per Liter
(a) AgIO ₃	6.5×10^{-3}
(b) Mg(OH) ₂	1.2×10^{-2}
(c) Hg ₂ I ₂	2.0×10^{-7}

5. What are the concentrations of Fe⁺⁺⁺ ion and OH⁻ ion in a liter of a saturated solution of Fe(OH)₃? $K_{s.p.}$ of Fe(OH)₃ is 1.1×10^{-36}

$$\text{Ans. } 4.5 \times 10^{-10} \text{ gram ion}$$

$$1.5 \times 10^{-9} \text{ gram ion}$$

6. Calculate the gram-ion quantity of Ba^{++} ion in 10.0 ml. of a saturated solution of BaCO_3 , the $K_{\text{s.p.}}$ being 8.1×10^{-9} .

7. What carbonate-ion concentration is required to start precipitation of the respective alkaline earth carbonates in liter solutions containing 100 milligrams of the respective metallic ions, the solubility-product constants being given?

<i>Ion</i>	$K_{\text{s.p.}}$	<i>Ans.</i>
(a) Ca^{++}	9.3×10^{-8}	(a) 3.7×10^{-5}
(b) Ba^{++}	8.1×10^{-9}	(b) 1.1×10^{-5}
(c) Sr^{++}	1.6×10^{-9}	(c) 1.4×10^{-6}

8. What sulfide-ion concentration is required to start the precipitation of the respective sulfides in 100-ml. solutions containing 50 milligrams of the respective metallic ions, the solubility-product constants being given?

<i>Ion</i>	$K_{\text{s.p.}}$
(a) Pb^{++}	3.0×10^{-28}
(b) Sn^{++}	1.0×10^{-26}
(c) Ni^{++}	1.4×10^{-24}
(d) Mn^{++}	1.0×10^{-15}
(e) Zn^{++}	1.2×10^{-23}

9. What OH^- ion concentration would be needed in order to start the precipitation of $\text{Mg}(\text{OH})_2$ in 5 ml. of solution containing 0.001 gram ion of Mg^{++} , the $K_{\text{s.p.}}$ being 3.5×10^{-11} ? *Ans.* 1.3×10^{-5}

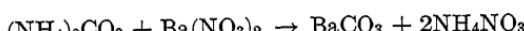
10. The qualitative test for calcium consists of producing a precipitate of calcium oxalate. The $K_{\text{s.p.}}$ of CaC_2O_4 is 2.6×10^{-9} . Suppose you have 5 ml. of a solution containing 50 milligrams of Ca, and you add 0.001 gram mole of $(\text{NH}_4)_2\text{C}_2\text{O}_4$. Show by a calculation whether or not the test for calcium will be obtained.

11. Will you get a precipitate of BaCrO_4 if to 5 ml. of the test solution containing 10 milligrams of Ba^{++} per ml. you add 5 ml. of K_2CrO_4 reagent (100 grams of K_2CrO_4 per liter)? The $K_{\text{s.p.}}$ of BaCrO_4 is 1.6×10^{-10} . Prove your answer by a calculation. *Ans.* Yes

12. Suppose that a sample for analysis is known to contain 0.5 gram of $\text{Pb}(\text{NO}_3)_2$, and the sample is dissolved in 20 ml. of water. If you take 2 ml. of the solution, what CrO_4^- ion concentration is necessary to reveal a test for lead? The $K_{\text{s.p.}}$ of PbCrO_4 is 1.7×10^{-14} . *Ans.* 2.3×10^{-13}

13. What is the hydroxyl-ion concentration necessary to satisfy the equilibrium relationship $C_{\text{Fe}^{++}} \times (\text{COH}^-)^2 = 1.6 \times 10^{-14}$ (a) in a solution containing 0.005 gram ion per liter of ferrous ion; (b) in a similar solution of ferric salt, the $K_{\text{s.p.}}$ being $C_{\text{Fe}^{+++}} \times (\text{COH}^-)^3 = 1.1 \times 10^{-36}$? *Ans.* 1.8×10^{-6}
 6.0×10^{-12}

14. Calculate the grams of $(\text{NH}_4)_2\text{CO}_3$ required in the following equation,



to react, stoichiometrically, with 10 ml. of test solution containing 0.0190 gram of $\text{Ba}(\text{NO}_3)_2$. When the calculated amount of $(\text{NH}_4)_2\text{CO}_3$ has been added, how much Ba^{++} and CO_3^{--} remain in the solution? The $K_{\text{s.p.}}$ of BaCO_3 is 8.1×10^{-9} .

15. If to a liter of solution containing 0.1 gram ion of Ag^+ ion enough Cl^- ion is added to make the concentration of Cl^- ion remaining in solution 1×10^{-6} gram ion per liter, how much AgCl has been precipitated? The $K_{\text{s.p.}}$ of AgCl is 1.1×10^{-10} . *Ans.* 14.32 gram

16. How many grams of NaCl must be added to 100 ml. of a solution which contains 0.020 gram of $\text{Hg}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ per liter, to start precipitation of Hg_2Cl_2 ? $K_{\text{s.p.}}$ of Hg_2Cl_2 is 2.0×10^{-18} .

17. In a solution in which SrSO_4 and BaSO_4 are being precipitated simultaneously, what is the ratio of Sr^{++} ion to Ba^{++} ion remaining in the solutions? $K_{\text{s.p.}}$ of SrSO_4 is 3.6×10^{-7} . $K_{\text{s.p.}}$ of BaSO_4 is 1.2×10^{-10} . *Ans.* 3000:1

18. If you wished to precipitate FeS but not MnS , what would have to be the sulfide-ion concentration in a solution containing concentrations of 0.01 of both metallic ions?

19. Calculate the ratio of the concentration of Pb^{++} ions to Hg_2^{++} ions in a solution to which enough HCl has been added to start precipitation of both PbCl_2 and Hg_2Cl_2 . *Ans.* 1.4×10^{-17}

20. A certain solution contains 0.01 gram ion each of Ni^{++} ion and Pb^{++} ion per liter. Between what limits should the sulfide-ion concentration be maintained if only PbS is to be precipitated?

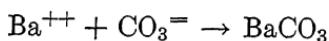
THE ALKALINE EARTH ELEMENTS: BARIUM (Ba^{++}), STRONTIUM (Sr^{++}), CALCIUM (Ca^{++}), MAGNESIUM (Mg^{++})

The properties of this closely related family of elements are described in the following pages, followed by a set of preliminary experiments which demonstrate their analytical relationships and furnish the basis upon which they are separated and detected. All belong to group II of the periodic table. The first three constitute group IV of the analytical scheme, which is designated the alkaline earth group or the ammonium carbonate group.

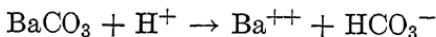
Magnesium is included here for study, since it resembles in many respects the other elements of this family. In the scheme of analysis used in this book, magnesium is not precipitated in group IV, its detection being reserved for group V along with the alkali metals.

BARIUM, Ba^{++}

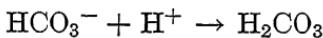
This element is always divalent and belongs to group II of the periodic table. Barium salts are colorless unless the anion is colored. The hydroxide is too soluble to be precipitated by NH_4OH or NaOH . Ammonium carbonate precipitates white BaCO_3 :



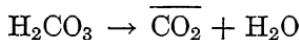
BaCO_3 is soluble in strong acids as well as in weak acids, such as $\text{HC}_2\text{H}_3\text{O}_2$ and H_2CO_3 . In the treatment with an acid, the bicarbonate ion, HCO_3^- , first forms



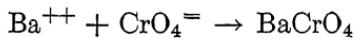
which then reacts to form unstable carbonic acid:



The carbonic acid decomposes into CO_2 and water:

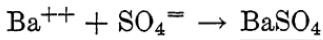


Barium chromate is precipitated when a chromate such as K_2CrO_4 is added to a barium salt solution:



BaCrO_4 is soluble in strong acids but insoluble in acetic acid. It is best precipitated from a slightly acid solution containing $\text{NaC}_2\text{H}_3\text{O}_2$. The precipitation of BaCrO_4 is the method customarily used for separating barium from strontium and calcium.

Barium sulfate is readily precipitated by dilute H_2SO_4 or a soluble sulfate such as $(\text{NH}_4)_2\text{SO}_4$:



The precipitate is very insoluble in water and in dilute acids. Barium is determined quantitatively by this reaction. BaSO_4 can be transformed into BaCO_3 by being boiled with Na_2CO_3 or, better still, by a fusion with solid Na_2CO_3 . This is a general method for getting insoluble residues into solution and is employed later in making an anion solution for systematic analysis.

The oxalate, BaC_2O_4 , is more soluble in water than the corresponding calcium and strontium oxalates. It is soluble in hot acetic acid and differs in this respect from CaC_2O_4 .

Inasmuch as, under certain circumstances, strontium chromate may precipitate and lead to false indications, the final identification of barium is based on a flame test, the color of the flame being green. The flame spectrum of barium as observed by means of a spectroscope permits a more precise identification.

Sodium rhodizonate has been suggested as a test for barium, the product having a red color. Strontium, however, interferes

with this test, but calcium does not. The use of this reagent has not found much favor, since its preparation is difficult and the reagent itself is quite unstable.

STRONTIUM, Sr⁺⁺

Strontium, like barium and calcium, is a divalent element. The reactions of the strontium ion are much like those of the other two alkaline earth elements. The carbonate, SrCO_3 , is readily precipitated by the group reagent, $(\text{NH}_4)_2\text{CO}_3$. The chromate is much more soluble than BaCrO_4 . Strontium sulfate, more soluble than barium sulfate but less soluble than calcium sulfate, is precipitated by dilute H_2SO_4 and soluble sulfates; strontium is separated from calcium by virtue of the smaller solubility of SrSO_4 . The solubility of the chromate as well as that of the oxalate is intermediate between the corresponding salts of barium and calcium.

The flame test usually is relied upon for the identification of strontium. The flame is a crimson or deep red.

CALCIUM, Ca⁺⁺

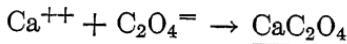
This alkaline earth element is very abundant and of considerable technical importance. It occurs widely as limestone (impure CaCO_3) and has many industrial uses when in the form of the carbonate or oxide (lime). The hydroxide, $\text{Ca}(\text{OH})_2$, is known as limewater.

The carbonate is quite insoluble and readily precipitated by ammonium or sodium carbonate. It is soluble in most acids, including dilute $\text{HC}_2\text{H}_3\text{O}_2$.

Calcium sulfate is soluble enough so that it ordinarily is not precipitated by a sulfate reagent of the usual strength. In a saturated solution of a calcium salt, there will be partial precipitation of CaSO_4 .

The chromate is very soluble. See the table of solubilities on page 82.

The most characteristic salt from an analytical standpoint is the oxalate, CaC_2O_4 . It is by precipitating this that calcium is separated from strontium.



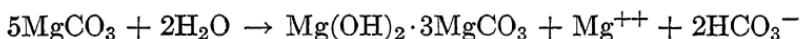
This reaction is likewise the basis of the quantitative determination of calcium. The reverse of this reaction is utilized in the precipitation of oxalates.

The color of the calcium flame is a yellowish red.

MAGNESIUM, Mg⁺⁺

Ammonium hydroxide and other soluble hydroxides, when added to a solution of a magnesium salt, produce a gelatinous precipitate of the sparingly soluble hydroxide, Mg(OH)₂. The presence of ammonium salts in sufficiently high concentration prevents the precipitation of Mg(OH)₂ by NH₄OH. Magnesium hydroxide is readily dissolved by acids, even those as weak as carbonic and acetic.

From concentrated solutions of magnesium salts, soluble carbonates produce a white precipitate of hydrated magnesium carbonate, MgCO₃·3H₂O. As with the hydroxide, no precipitate forms in the presence of ammonium salts. Over a wide range of temperature the reaction with water is approximately expressed by the following equation:



This basic carbonate also is precipitated from solutions too dilute to give a precipitate of the carbonate.

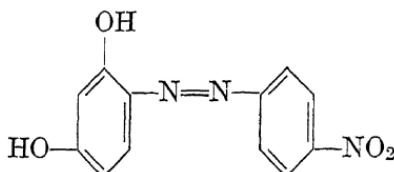
From an analytical standpoint the most important salt of magnesium is magnesium ammonium phosphate, MgNH₄PO₄, a white finely crystalline precipitate, which forms according to the equation,



in an ammoniacal solution in the presence of an ammonium salt such as NH₄Cl. The reaction is used as the basis for the detection, as well as the quantitative determination, of magnesium. Conversely, the same reaction may be utilized for the detection and determination of phosphates, and an analogous reaction with the arsenate AsO₄⁼ ion serves as a method for the detection of arsenic.

A sensitive test for magnesium is the formation of a "lake" or "adsorption complex" with the dye, paranitrobenzene azoresorcinal.

The organic compound has the structure shown by the formula:



In an alkaline solution, $Mg(OH)_2$ first forms and then adsorbs the dyestuff, producing a deep blue color.

In the systematic scheme of analysis, magnesium is detected separately in group V.

PRELIMINARY EXPERIMENTS

1. Action of Ammonium Carbonate. In one test tube place 2 drops of Ba^{++} test solution; in another put 2 drops of Sr^{++} test solution, and in a third, 2 drops of Ca^{++} test solution. To each, add 1 drop of dilute ammonia solution. The slight turbidity which may form is not due to the formation of hydroxides but rather to traces of carbonate ion which may have contaminated the ammonia reagent.

Now add 1 or 2 drops of $(NH_4)_2CO_3$ reagent. What are the precipitates which form? Write in your notebook the ionic equations for their formation.

2. Action of Potassium Chromate. Dissolve the precipitated carbonates by adding, dropwise, dilute 0.1 M acetic acid to each. Then add a drop of K_2CrO_4 reagent to each. Do you get a precipitate in each case? Particularly, in what respect does barium differ from calcium, and strontium from barium? Record the result and write equations.

3. Action of Ammonium Sulfate. As in the first experiment, treat a few drops of the test solutions of Ba^{++} , Sr^{++} and Ca^{++} with $(NH_4)_2SO_4$ reagent. Describe the results. $SrSO_4$ is more soluble in water than $BaSO_4$, but not nearly so soluble as $CaSO_4$. This fact is utilized to make a fairly satisfactory separation of strontium from calcium.

As a separate experiment, add a few drops of saturated $CaSO_4$ solution to a few drops of Sr^{++} test solution. Does $SrSO_4$ form?

4. Behavior toward Ammonium Oxalate. To 2 drops of the 3 ions in separate tubes, add a drop of dilute ammonia solution and then a drop of $(NH_4)_2C_2O_4$ reagent. In what test solution does the oxalate precipitate most readily? Write the equation. This reaction serves to separate calcium from strontium.

Try to dissolve the precipitates by adding dilute acetic acid until the solutions show an acid reaction toward litmus paper, and then heat the tubes. What conclusion can you draw concerning the solubility of these oxalates in hot dilute $H_2C_2H_3O_2$?

5. Flame Tests. The flame tests for barium, strontium and calcium are very important in identifying these ions and should be studied carefully. Dip a clean looped platinum wire into a solution of a barium salt and hold it in the

outer portion of a Bunsen or Meker flame. Note the color which appears after a short time. Intensify the color by dipping the wire into concentrated HCl contained in a test tube and then replacing it in the flame. Repeat, alternately, dipping in test solution and in concentrated HCl, and heating if the color is not produced on the first trial.

Clean the wire by alternately dipping it in HCl and heating it until it no longer colors the flame. With the clean wire, repeat the procedure, using a strontium compound. Describe the color of the strontium flame.

Repeat again, using a calcium compound. Distinguish the color of the calcium flame from that of strontium. Then carry out the tests, using the salts in pairs, until the appearance of the flames due to the mixtures can be distinguished clearly.

6. Non-Precipitation of $Mg(OH)_2$ and $MgCO_3$ in Ammonium Chloride Solutions. To a drop of $Mg(NO_3)_2$ test solution add a few small crystals of NH_4Cl , and then add NH_4OH . Repeat the experiment, omitting the NH_4Cl . In which solution does precipitation occur?

Repeat the experiment, using $(NH_4)_2CO_3$ as the precipitating agent; add NH_4Cl in one case, and omit it in the other. The white precipitate in the one case is the basic carbonate of magnesium. Write the equation.

7. Phosphate Test for Magnesium. Place a drop of magnesium test solution in a centrifuge tube and make ammoniacal with NH_4OH . Add particles of solid NH_4Cl , shaking until the precipitate of $Mg(OH)_2$ disappears, and then add a drop of disodium hydrogen phosphate solution. What forms? Write the equation for the reaction. Although this is the least soluble inorganic salt of magnesium and is less soluble in NH_4OH than in water, complete (quantitative) precipitation occurs only after it has been shaken and allowed to stand for some time, inasmuch as the salt readily forms a highly supersaturated solution.

8. Paranitrobenzene Azoresorcinol Test for Magnesium. To a drop of magnesium test solution on a spot plate or in a test tube add 2 drops of the alkaline dye solution. Observe the change in color. Explain the phenomenon.

9. Separation and Verification of Barium, Strontium and Calcium (Optional). Prepare a mixture of these 3 elements by taking 5 drops of each of the stock test solutions. Dilute to 1 ml. Make ammoniacal with dilute ammonia solution, warm in the water bath, and add $(NH_4)_2CO_3$ reagent until precipitation is complete. Centrifuge. The precipitate consists of $BaCO_3$, $SrCO_3$ and $CaCO_3$. Write the ionic equations by which these carbonates are formed.

Dissolve the mixed carbonates with dilute acetic acid, add 10 drops of sodium acetate, and then add potassium chromate. Centrifuge, reserving the centrifugate. What is the yellow precipitate? Verify the presence of barium by dissolving in HCl and by carrying out a flame test.

Add $(NH_4)_2SO_4$ reagent to the centrifugate. What is the white precipitate? Prove that it contains strontium by the flame test. What is the color of the flame? This separation of strontium from calcium may be only partial; a modification is introduced under the procedure for this group.

Centrifuge off the precipitate, neutralize the solution, and add $(NH_4)_2C_2O_4$ reagent. What is the precipitate? To confirm the presence of calcium, centrifuge, and dissolve the residue in dilute HCl and carry out a flame test.

REVIEW EXERCISES. THE ALKALINE EARTH METALS

1. Why are the members of this group precipitated as carbonates rather than as sulfates, chromates or oxalates? Group together the reactions occurring during the group precipitation.
2. How do Ba^{++} , Sr^{++} and Ca^{++} ions behave toward K_2CrO_4 ? Explain how a separation might here be made.
3. In what reagents are the following soluble: (a) BaCO_3 ; (b) CaCrO_4 ; (c) BaCrO_4 ?
4. By what means would you put BaSO_4 into solution? Give the equations for the reactions.
5. Will $(\text{NH}_4)_2\text{SO}_4$ precipitate CaSO_4 equally as well as it will precipitate SrSO_4 ? Will a saturated CaSO_4 solution form a precipitate of SrSO_4 as readily as it will form a precipitate of CaSO_4 ?
6. Given a solution which contains equal amounts of Sr^{++} and Ca^{++} ions, which reagent would you add, $(\text{NH}_4)_2\text{SO}_4$ or saturated CaSO_4 , in order to precipitate SrSO_4 in preference to CaSO_4 ? Explain what is meant by fractional precipitation.
7. Calculate the ratio of Ca^{++} ions to Ba^{++} ions in a mixed solution at the point when both CaSO_4 and BaSO_4 are being precipitated.
8. Describe the flame tests of the elements in this group. Why are these flame tests so important here?
9. How would you prevent magnesium from precipitating as $\text{Mg}(\text{OH})_2$ or as MgCO_3 ? Why is this element not regularly a member of the ammonium carbonate group?
10. Describe two tests for magnesium.

OUTLINE OF METHOD OF ANALYSIS OF GROUP IV

This group consists of Ba^{++} , Sr^{++} and Ca^{++} ions. From an inspection of Table IV, which gives the solubilities of the carbonates, chromates, sulfates and oxalates of the members of this group, it can be seen that the carbonates are uniformly the least soluble; for this reason the group is precipitated as the carbonates with $(\text{NH}_4)_2\text{CO}_3$ reagent.

TABLE IV

SOLUBILITIES OF ALKALINE EARTH SALTS

Milligrams per 1 Ml. of Water, at Room Temperature

	Carbonate	Chromate	Sulfate	Oxalate
Barium	0.023	0.0038	0.023	0.086
Strontium	0.011	1.20	0.11	0.046
Calcium	0.013	4.00	2.10	0.0056

In order to prevent as far as possible the precipitation of MgCO_3 as well as of $\text{Mg}(\text{OH})_2$, a measured amount of NH_4Cl is added with

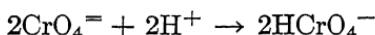
the $(\text{NH}_4)_2\text{CO}_3$ during the group precipitation. The presence of NH_4Cl prevents the solubility-product constant of $\text{Mg}(\text{OH})_2$ from being reached, since the OH^- ion concentration is not sufficiently high (the theory involved is explained in detail in Chapter V). MgCO_3 , likewise, does not precipitate in any appreciable amount, because the excess of NH_4^+ ion reduces the $\text{CO}_3^{=}$ ion concentration by virtue of the reaction,



to such an extent that the $K_{s.p.}$ of MgCO_3 (a relatively large constant) cannot be reached. The solubility-product constants of BaCO_3 , SrCO_3 and CaCO_3 easily are exceeded, and precipitation of these three carbonates takes place readily. Upon centrifugation, the supernatant liquid will contain Mg^{++} , Na^+ and K^+ if these are present in a sample, as well as the NH_4^+ ion.

The carbonates are dissolved in dilute acetic acid in order that a separation of barium from strontium and calcium may be effected.

The table further suggests that the relatively slight solubility of BaCrO_4 compared to SrCrO_4 and CaCrO_4 offers the means of separating barium from strontium and calcium. The preliminary experiments have shown that BaCrO_4 is precipitated from an acetic acid solution containing $\text{NaC}_2\text{H}_3\text{O}_2$ whereas SrCrO_4 is not. The function of the acetic acid and $\text{NaC}_2\text{H}_3\text{O}_2$ is to convert a portion of the $\text{CrO}_4^{=}$ ion into bichromate ion, HCrO_4^- , and possibly dichromate ion, $\text{Cr}_2\text{O}_7^{=}$, in accordance with the equations:



and



Hence if K_2CrO_4 is added, practically all of the barium is precipitated as BaCrO_4 , and little or no SrCrO_4 is formed. Provided then that the amount of Sr^{++} ion is not excessively high, a fairly complete separation of barium from strontium can be made. The identity of barium in the precipitate is verified by the flame test.

On further inspection of the table we discover the fact that SrSO_4 is relatively less soluble than CaSO_4 . The difference, however, in the solubilities is not great enough to make a sharp separation of strontium from calcium by the use of $(\text{NH}_4)_2\text{SO}_4$. We encounter here a special case of fractional precipitation in the partial separation of Sr^{++} from Ca^{++} .

The solubility-product constant of SrSO_4 is 3.6×10^{-7} , and that of CaSO_4 is 2.2×10^{-4} . SrSO_4 therefore will begin to precipitate before CaSO_4 when $\text{SO}_4^{=}$ ions are added to a solution containing both Sr^{++} and Ca^{++} ions. CaSO_4 will begin to precipitate along with SrSO_4 when the concentrations of Sr^{++} and Ca^{++} remaining in solution bear a ratio to each other proportional to the ratio of their respective solubility-product constants:

$$\frac{K_{\text{s.p.}} \text{ SrSO}_4}{K_{\text{s.p.}} \text{ CaSO}_4} = \frac{3.6 \times 10^{-7}}{2.2 \times 10^{-4}} = \frac{C_{\text{Sr}^{++}}}{C_{\text{Ca}^{++}}} = \frac{1}{610}$$

The ratio is 1:610. This means that a precipitate of pure SrSO_4 will continue to form until the ratio of the concentrations is reduced to the afore-mentioned value, that is, for every strontium ion remaining there will be 610 calcium ions left in solution. After this ratio is obtained, both SrSO_4 and CaSO_4 will precipitate simultaneously. The precipitate obtained in adding $(\text{NH}_4)_2\text{SO}_4$ is therefore apt to contain some CaSO_4 as well as SrSO_4 . Enough calcium ion, however, will remain unprecipitated for it to be separated in the centrifuge from the sulfate precipitation. The presence of strontium in the sulfate precipitate must be confirmed by the flame test.

The calcium remaining in the centrifugate from the sulfate precipitation is precipitated with $(\text{NH}_4)_2\text{C}_2\text{O}_4$, and for final confirmation the flame test is utilized.

TABLE V
DIAGRAMMATIC OUTLINE OF ANALYSIS OF GROUP IV

<i>Solution</i>	<i>Precipitate</i>	<i>Precipitate</i>	<i>Precipitate</i>	<i>Prelim.</i>	<i>SrSO₄</i>
Ba^{++}	<u>BaCO_3</u>		<u>BaCrO_4</u> Yellow— Confirm by green flame		
Sr^{++}	Add NH_4Cl NH_4OH $(\text{NH}_4)_2\text{CO}_3$ Centfg.	<u>SrCO_3</u>	Add $\text{HC}_2\text{H}_3\text{O}_2$ $\text{NaC}_2\text{H}_3\text{O}_2$ K_2CrO_4 Centfg.	Sr^{++} NaOH Na_2CO_3 Centfg. Dissolve in $\text{HC}_2\text{H}_3\text{O}_2$ Ca^{++}	Sr^{++} CaSO_4 $(\text{NH}_4)_2\text{SO}_4$ Centfg. $(\text{NH}_4)_2\text{C}_2\text{O}_4$ <u>CaC_2O_4</u> Confirm by orange-red flame
Ca^{++}		<u>CaCO_3</u>			

PROCEDURE FOR THE ANALYSIS OF GROUP IV

Group Precipitation. Place 1 ml. of the sample in a centrifuge tube, add 10 drops of NH_4Cl reagent, made alkaline by adding a tiny drop of concentrated ammonia solution, and then add $(\text{NH}_4)_2\text{CO}_3$ reagent until precipitation appears complete. This may require 10 or more milliliters. Warm but do not boil the precipitate in the water bath for 5 minutes; this is to coagulate the precipitate. Centrifuge, and test the supernatant liquid for complete precipitation by adding a drop or two more of the reagent. Centrifuge again. Pipet off, and reserve the centrifugate for the analysis of group V; it may contain magnesium, sodium and potassium, and, of course, it contains ammonium salts. The purpose of the NH_4Cl in the group precipitation is to prevent magnesium from precipitation here.

The residue may contain BaCO_3 , SrCO_3 and CaCO_3 . Wash this with 5 drops of water, stir, and centrifuge.

Separation and Detection of Barium. Dissolve the residue in the least possible amount of dilute $\text{HC}_2\text{H}_3\text{O}_2$, using portions of 5 drops of the reagent until the carbonates are dissolved. Add 10 drops of sodium acetate solution, dilute to 2 ml., warm, and then add potassium chromate solution until precipitation is complete. Centrifuge, remove, and reserve the supernatant liquid. The yellow residue is probably BaCrO_4 and indicates the presence of barium.

To confirm the presence of barium, wash the yellow precipitate with a few drops of water, centrifuge, and dissolve the residue by treating it with a few drops of concentrated HCl. This is done in order to convert the BaCrO_4 into a soluble form, in which condition it gives a more satisfactory flame test. Clean the platinum wire, bend the end into a loop, and dip the wire into the barium solution; heat it in the outer portion of the non-luminous flame. A green color appearing after heating for a few seconds proves the presence of barium. If the color is not obtained in the first trial, dip the wire again into clean HCl, and reheat; repeat dipping into the solution, heating, and applying the acid treatment several times if necessary.

Separation and Detection of Strontium. In order to remove the excess of the chromate reagent, take the centrifugate from the BaCrO_4 separation, make it alkaline with NaOH, heat in water bath, and add Na_2CO_3 reagent. This will reprecipitate SrCO_3 and

CaCO_3 . Centrifuge and wash the residue repeatedly, pipeting off and discarding the supernatant liquid until it is no longer yellow. Dissolve the carbonates with dilute $\text{HC}_2\text{H}_3\text{O}_2$.

A preliminary test is now made for strontium, by adding a drop of saturated CaSO_4 solution to a few drops of the dissolved carbonates. If a white precipitate forms, strontium is probably present in the sample; if not pass on to the detection of calcium. In the probable presence of strontium, treat the remainder of the solution with $(\text{NH}_4)_2\text{SO}_4$ reagent until precipitation appears complete. Heat 5 to 10 minutes in the water bath. Centrifuge. A residue is mostly if not entirely SrSO_4 ; the centrifugate may contain calcium.

The precipitate may not be pure SrSO_4 . Some CaSO_4 may have precipitated, along with the SrSO_4 . The separation of strontium therefore is not sharp. The precipitate must be proved to contain strontium by a flame test. The color should be a crimson or rich red.

Detection of Calcium. To the centrifugate from the strontium separation add a drop of ammonia solution and then $(\text{NH}_4)_2\text{C}_2\text{O}_4$ reagent. If a precipitate forms, calcium is probably present. When precipitation is complete, centrifuge the solution.

Dissolve the precipitate in 2 or 3 drops of dilute HCl. Carry out a flame test. A yellowish red flame confirms the presence of calcium.

OUTLINE OF METHOD OF ANALYSIS OF GROUP V

This group properly includes the alkali metals, sodium and potassium, together with magnesium. Provision is made here for the detection of the ammonium ion. The group is also called the soluble cation group, because there is no single reagent which will precipitate these ions. Consequently individual tests must be made for each element.

In a systematic analysis magnesium is deliberately prevented from precipitating in groups III and IV. The theory of the non-precipitation of $\text{Mg}(\text{OH})_2$ and MgCO_3 cannot be fully discussed or understood at this time; the complete explanation is taken up in Chapter V. A precipitation test (MgNH_4PO_4) and the "lake" test are recommended as tests for magnesium.

Although flame tests for sodium and potassium are the most convenient ones for these two elements, an additional precipitation test for each is suggested.

The test for the ammonium ion must be conducted on a portion of the original sample, since, obviously, through the use of ammonium compounds in previous group precipitations, the centrifugate from group IV will have been contaminated with the ammonium ion.

TABLE VI

DIAGRAMMATIC OUTLINE OF ANALYSIS OF GROUP V

<i>Solu-</i> <i>tion</i>		
NH_4^+	Add HNO ₃ Evap. to dryness, add water and HCl Use separate portions	—Test for NH ₄ in portion of original sample with NaOH → blue on litmus. —Nitrobenzene azoresorcinol + NaOH → blue lake Confirm with Na ₂ HPO ₄ + NH ₄ OH → <u>MgNH₄PO₄</u> —Na ₃ Co(NO ₂) ₆ → K ₂ NaCo(NO ₂) ₆ yellow Confirm with flame test —Zinc uranyl acetate → yellow ppt. Confirm with flame test.
Mg^{++}		
K^+		
Na^+		

PROCEDURE FOR THE ANALYSIS OF GROUP V

The centrifugate reserved from the precipitation of group IV may contain magnesium, potassium and sodium, and possibly traces of alkaline earth ions; it will contain the ammonium ion, because (NH₄)₂CO₃ and NH₄Cl were introduced in the preceding group precipitation. The test for the NH₄⁺ ion as a constituent of the sample must be made on a portion of the original sample reserved for this purpose. The test follows:

Since there is no group precipitating reagent for this group, individual tests must be made for each ion. To remove any alkaline earth ions which may have failed to precipitate in group IV, add a drop of (NH₄)₂SO₄ and one of (NH₄)₂C₂O₄ reagent. Centrifuge if a precipitate forms; discard the residue.

Removal of Ammonium Salts. Since the lake test for magnesium and the precipitation test for potassium are interfered with by ammonium salts, the latter must be removed. Transfer the centrifugate now free from alkaline earth ions, to a crucible; boil until salts crystallize out. Add 15 to 20 drops of concentrated HNO₃, and evaporate cautiously to dryness under the hood. Continue heating carefully to avoid spattering, until NH₃ fumes are no longer given off. After the crucible has cooled, add 15 drops of water and

1 drop of dilute HCl; stir with the platinum wire. Warm the residue if it does not dissolve readily; add a little more water if necessary. Use this solution when free from ammonium salts, for tests for Mg, K⁺ and Na⁺ ions.

Detection of Magnesium. Place a drop of the solution on a spot plate and add a drop of the nitrobenzene azoresorcinol reagent and a small drop of dilute NaOH. A light blue precipitate shows the presence of magnesium.

This test should be confirmed by adding to 5 drops of the centrifuge a few drops of dilute ammonia and 3 drops of Na₂HPO₄ reagent. The appearance of white crystals of MgNH₄PO₄, which may be slow in forming, confirms magnesium.

Detection of Potassium. Place a drop of the solution on a spot plate, and add a little finely powdered Na₃Co(NO₂)₆. A yellow precipitate indicates the presence of potassium.

Dip a clean platinum wire into the remaining solution, and conduct the flame test, viewing the flame coloration through a blue glass plate. A reddish flame surrounded by blue proves the presence of potassium.

Detection of Sodium. Add 5 drops of zinc uranyl acetate solution to 1 drop of the solution in a centrifuge tube. A pale yellow precipitate, which may come out slowly, shows the presence of sodium. A brilliant persistent yellow flame, if observed in conducting the test for potassium, shows the presence of appreciable amounts of sodium.

Detection of the Ammonium Ion. Place a small amount of the original sample in a small beaker and carry out the test as described on page 53.

CHAPTER IV

THE ELEMENTARY THEORY OF OXIDATION AND REDUCTION. THE THEORY OF AMPHOTERISM. THE THEORY OF COMPLEX IONS. THE ELEMENTS OF GROUP III

This chapter introduces 7 important elements, whose properties and reactions strikingly illustrate the important phenomena of oxidation and reduction, amphotericism and complex-ion formation. In the analytical procedure of separation, the cations of iron, manganese, aluminum and chromium are precipitated with ammonia as hydroxides; these constitute division *A*, or the ammonium hydroxide subgroup of group III. Nickel, cobalt and zinc subsequently are precipitated as sulfides with hydrogen sulfide; this subgroup is designated division *B* or the ammonium sulfide subgroup of group III.

Zinc exists only in the divalent state, and aluminum is always trivalent. The other 5 elements in this analytical group exist in two or more valence conditions or states of oxidation. This is a fine opportunity, therefore, to present an introductory discussion of valence as related to oxidation and the writing of equations for *redox* reactions. The hydroxides of aluminum, chromium and zinc possess amphoteric properties, and hence this phenomenon logically can be introduced here. These two phenomena are discussed along with the properties and prescribed laboratory work of group IIIA in the first part of this chapter. Complex-ion formation, so characteristic of nickel, cobalt and zinc, is considered in the second part, together with the properties and preliminary experiments of these three elements. This is followed by the procedure for the analysis of this group as a whole.

ATOMIC STRUCTURE AND VALENCE. *Redox* REACTIONS AND EQUATIONS

One of the most fundamental problems in chemistry is the determination of the nature of chemical union. Ever since knowledge

of the properties and behavior of the electron first was applied to the explanation of chemical phenomena, the problem has been one of showing how the electron functions in forming chemical bonds, that is, in producing what we call "valence." The interpretation of valence in terms of electrons is, in its simple aspects, so easily understood and has been so successful in explaining many chemical facts that it is now introduced into practically every elementary course in chemistry. For this reason some of the following discussion will be familiar to the student; it is repeated here to serve as a review and as an introduction to the phenomenon of oxidation and reduction.

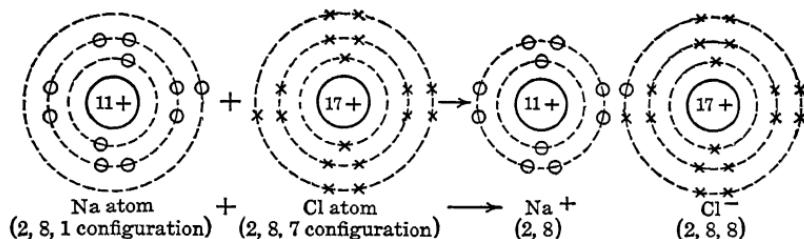
The Structure of Atoms. An atom may be visualized as a miniature solar system. A small very dense nucleus takes the place of the sun, and a number of electrons, called planetary electrons, move about it after the fashion of planets. Each electron constitutes a negative charge of 1.59×10^{-19} coulomb, a coulomb being the amount of electricity represented by a current of 1 ampere flowing for 1 second. The amount of electricity represented by the electronic charge commonly is referred to as a unit of negative charge; the corresponding quantity of positive electricity constitutes a unit of positive charge. The nucleus, which provides practically all the mass of the atom, is made up of units of positive electricity (protons), together with electrons. In the nucleus the electrons are bound to an equal number of protons, producing neutrons; the excess protons remain as unbound positive charges. The number of unbound protons in the nucleus is the atomic number of the element. The total number of planetary electrons in the orbits or shells equals the number of excess protons in the nucleus, thus making the atom, as a whole, electrically neutral.

Types of Valence Bonds. Atoms of elements which do not have a stable valence group like that of one of the inert gases have a tendency to attain such a configuration; their chemical properties then are largely determined by the magnitude of the tendency and the manner of attaining the configuration. An atom may secure a stable valence group in either of two general ways:

1. By capturing from one or more atoms enough electrons to make a total of 8, in the valence group, or by losing to other atoms all the electrons in its own valence group. In the latter case the atom reverts to the next lower stable configuration.
2. By sharing electrons with another atom or with each of several other atoms, each electron so shared being counted in

the valence group of each of the two atoms involved in the sharing.

The Formation and Structure of Simple Ions. If a stable group is formed, by capturing or losing electrons, there is an actual transfer of electrons from one atom to another. This transfer leaves the donor atoms positively charged and gives the acceptor atoms a negative charge, forming cations and anions, respectively. The following equation for the formation of a sodium ion and a chloride ion from an atom of Na and an atom of Cl illustrates such a transfer:



This representation is not to be interpreted too literally. The use of different symbols (circles and crosses) to represent the electrons belonging to sodium and to chlorine does not signify a difference in the nature of the electrons; the purpose is merely to simplify the visualization of the electron transfer. Also, the distribution about the atom is not intended to represent the spatial relations of the electrons to the nucleus in an actual atom; it is simply a means of representing pictorially the successive electronic groups and the number of electrons in each group.

It will be noticed that the single electron in the valence shell of the sodium atom has been transferred to the valence shell of the chlorine atom, forming a sodium ion and a chloride ion, each of which has a stable group of 8 electrons in the outer orbit. A crystal of NaCl is an aggregate of such ions. It should be emphasized that in compounds of this type the ions are not formed upon the material being dissolved but are already present in the solid compound. The process of solution involves primarily a separation of the ions, allowing them to act more independently than they can in the crystal.

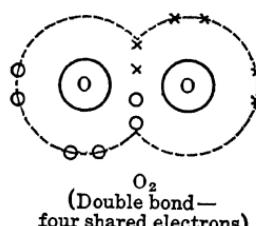
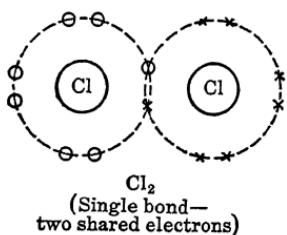
A valence bond formed in this way is called an ionized or polar bond, and this type of valence is called electrovalence, ionized valence or polar valence. Each electron transferred gives one unit of electrovalence to each of the two atoms concerned in the

transfer; the number of such units per atom constitutes the electro-valence of the element.

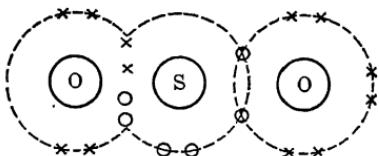
The electropositive elements are those in which the tendency to lose electrons is greater than the tendency to gain electrons in securing a stable group. This is the situation, in general, when the number of electrons in the valence group is less than 4, as it is in most of the metals. If the tendency to gain electrons is greater than the tendency to lose them, the element is electronegative. This happens, in general, when there are 6 or 7 electrons in the valence group, as in many of the non-metals. Elements which have 4 or 5 electrons in the valence group, as well as some elements with 3 or 6 or occasionally some other number, in general show little tendency either to gain or lose electrons and hence rarely form ionized compounds.

When the symbol for a simple ion, Na^+ , for example, is written, this does not imply that the sodium atom is associated with only one positive charge; quite to the contrary, it means that there is a surplus of one positive charge over the total number of negative charges (electrons) in the ion. Actually the sodium ion consists, as shown in the structural electronic diagram, of 10 electrons in the two shells and 11 protons or positive charges in the nucleus.

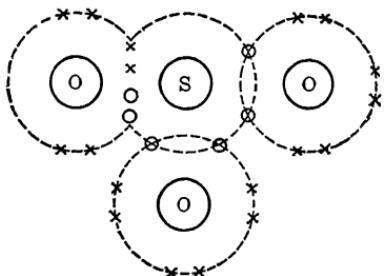
Covalence and Co-ordinate Valence. Attainment of a stable group by sharing electrons results in the formation of either covalent or co-ordinate covalent bonds. Covalent bonds are sometimes called non-polar or homo-polar bonds, and co-ordinate covalent bonds are sometimes called semi-polar or, frequently, simply co-ordinate bonds. In this book the term co-ordinate bond will be used. Each pair of shared electrons may be considered to constitute a single bond. In a covalent single bond one of the two shared electrons comes from each of the two atoms. This is illustrated by the following diagrams of the chlorine and oxygen molecules. For simplicity, all the electrons except those in the valence group have been omitted in these and all subsequent atomic diagrams.



If, instead of each atom supplying one of the two shared electrons, both of the electrons come from the same atom, the result is a co-ordinate bond, and each pair of electrons so shared constitutes 1 unit of co-ordinate valence. This is illustrated in the following diagram of SO_2 .



The oxygen atom shown on the right in this diagram is joined to the sulfur by a co-ordinate bond; the one on the left is joined by a covalent double bond. It will be noted that the sulfur atom has another pair of unshared electrons which, presumably, should be able to form a co-ordinate bond with another oxygen atom. In the SO_3 molecule this additional bond is formed, as is shown in the following diagram.



The diagram of the SO_2 molecule shows that more than one type of valence bond may exist in the same molecule and indicates the difficulty of stating the "valence" of an element or group unless the type of valence concerned is specified. Thus, whereas sulfur in SO_2 usually is considered to have a "valence" of 4, this valence really consists of a covalence of 2 and a co-ordinate valence of 1. For convenience, the number 4 may be called the "apparent valence" or "valence number" of sulfur in SO_2 ; similarly, in SO_3 the apparent valence of the sulfur is +6.

Valence Bonds and Ionization. When a substance containing polar bonds is dissolved in a polar solvent such as water, the polar bonds are broken and the ions move about more or less independently of each other. This is equivalent to saying that compounds having polar bonds are completely ionized in solution,

as they are in the solid state. On the other hand, covalent and co-ordinate bonds usually are not broken in solution. This means that atom groups which are held together by shared-electron bonds usually will remain intact and act as units in solution. The fact that the sulfate, phosphate and similar ions act as units in many chemical reactions is explained on this basis. Complex ions are discussed on page 127.

Although a compound may contain no polar bonds and thus be undissociated or non-ionized in the pure condition, it may be considerably ionized when dissolved in a polar solvent such as water, owing to the attraction of the polar-solvent molecules for the atoms of the compound.

Variable Valence. Only a few of the elementary features of this interesting subject can be mentioned here. The observant student already has noticed that the number of electrons in the outermost orbit of the atom is not always the same as the number of the group in which the element is found in the periodic table. He also may have discovered that, in many cases, if 8 is subtracted from the number of electrons in the next lower orbit, and if this difference is added to the number in the outermost orbit, the result will be the normal valence group of the element. To illustrate, uranium has the configuration 2-8-18-32-18-12-2 and appears in periodic group VI. If 8 electrons are subtracted from the group containing 12, the difference plus the 2 electrons in the last group totals 6.

The preceding discussion suggests the possibility that electrons may shift into the valence orbit from the orbit next to it and thereby change the valence of the element. This is essentially what occurs when an element changes from one ionized valence to another. For instance, Fe corresponds to the configuration 2-8-14-2. If the 2 valence electrons are lost, a ferrous ion, Fe^{++} , results. Loss of 3 electrons in this case results in the formation of a ferric ion, Fe^{+++} . Elements such as K, Ca, Al have a stable group of 8 electrons in the orbit next to the valence orbit. There is therefore a negligible tendency for electrons to be transferred into the valence group, and these elements accordingly exhibit only one valence state.

The shift of electrons from one orbit to another corresponds to the absorption or emission of light or other form of radiant energy. Compounds of metals of variable valence are almost invariably colored, whereas those of constant valence are usually colorless.

The phenomenon of color in compounds therefore corresponds to the ease with which electrons shift from one orbit to another in the atoms.

Oxidation–Reduction and Valence. As already has been mentioned, the unmodified word “valence” often is used inaccurately to represent a combination of several types of chemical bonds. For instance, we frequently refer to the valence of Mn in KMnO_4 as +7; of Cr in K_2CrO_4 as +6, and so on, the number being arrived at by equating the positive and negative valences of the elements in the compound.

The value obtained is important when used in connection with oxidation–reduction reactions, as is pointed out later. We shall refer to it as an “average” or “apparent” valence, or as the “valence number” or “oxidation number” of the element concerned. All of these terms are in more or less general use, but in this book we shall prefer the term “apparent valence.”

An increase in apparent valence corresponds to a loss of electrons, and a decrease to a gain of electrons. This is true whether the original apparent valence is positive or negative, provided the increase is considered algebraically; that is, if the original apparent valence is negative, an increase corresponds to a decrease in the numerical value. To illustrate, a change in apparent valence from +6 to +3 is an algebraic decrease and represents a reduction.

The Phenomena of Oxidation and Reduction. When an atom or ion loses one or more electrons (negative charges), there is an apparent net increase in the number of positive charges remaining, or an apparent net decrease in the number of negative charges remaining. Oxidation accordingly is defined as the loss of electrons by an atom or ion. Conversely, when an atom or ion accepts one or more electrons there is a decrease in the net positive charges. This phenomenon is called reduction: Reduction is the gain of electrons.

We have just seen how ions are formed from neutral atoms. For example, it has been pointed out that the neutral sodium atom, by losing an electron, is transformed into a sodium ion. The change can be expressed as an equation involving an electron in addition to chemical entities:



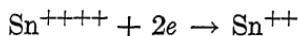
Likewise, the neutral atom of chlorine becomes a chloride ion by gaining an electron, a change which can be written thus:



In general, the metallic elements yield simple cations, that is, positively charged ions, when the neutral atom loses one or more electrons, and are therefore oxidized from the atomic state to the ionic form; conversely, metallic ions in accepting electrons may be reduced to the metallic (atomic or neutral) state. The non-metallic elements, on the other hand, particularly sulfur and the halogens, are reduced to simple anions when their neutral atoms gain electrons. These are examples of oxidations and reductions, respectively.

Oxidation and reduction are by no means confined to the change from the atomic state to the ionic state or vice versa. In fact, the most important and numerous cases of oxidation and reduction are those in which there is a change from one ionic form to another ionic form of the same element. Elements which have variable valence and therefore exist in two different ionic states are the ones which are involved in most of the oxidation and reduction reactions in qualitative analysis and which furnish some of the most useful oxidizing and reducing agents. Among the metallic elements (in the cation scheme) which show variable valence may be mentioned iron, nickel and cobalt; manganese, chromium; arsenic, antimony and bismuth; tin and lead; mercury and copper.

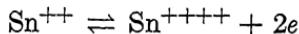
Tin, for example, is divalent as well as tetravalent; the stannous ion, Sn^{++} , can be oxidized to the stannic form, Sn^{++++} , and conversely stannic ions can be reduced to Sn^{++} . For the reduction of Sn^{++++} the electron equation is



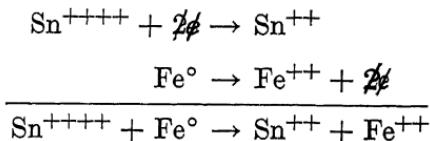
and, for the oxidation of Sn^{++} , the reverse electron equation is



Since these reactions are reversible, the equations can be combined into the single equation:

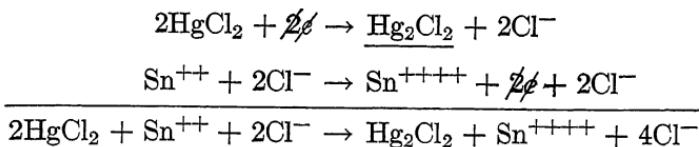


A suitable reducing agent for the stannic ion is metallic iron. The complete equation then is

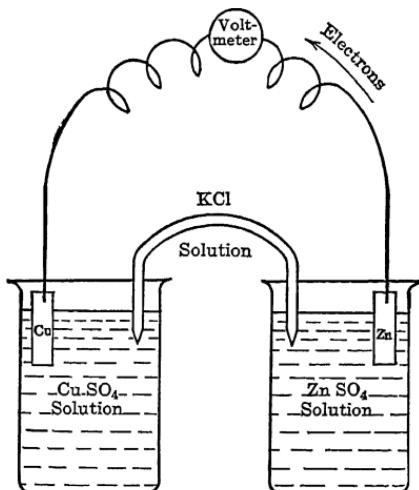


which shows the transfer of 2 electrons from the neutral atom of Fe to the Sn^{++++} ion.

Mercuric chloride will oxidize stannous chloride, itself being reduced to insoluble mercurous chloride, the formula of which is Hg_2Cl_2 . Since mercuric chloride is a weakly ionized salt and mercurous chloride is a precipitate, this equation is best written:



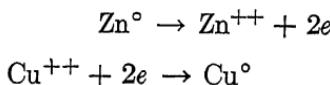
Any oxidation-reduction reaction can be expressed as the sum of two separate equations, one involving only oxidation and the



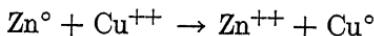
other only reduction. Moreover, except for experimental difficulties in some cases, any oxidation-reduction process can be carried out as two separate processes taking place *simultaneously but not necessarily in the same place*. An arrangement for accomplishing this experimentally is as follows. The oxidizing agent and the reducing agent (if it is assumed that they are both in solution) are placed in separate containers and connected by a salt bridge. This bridge consists of a narrow tube containing an electrolyte, a solution of KCl for example, with one end in the oxidizing solution and the other in the reducing solution. If now a suitable electrode, say a platinum plate, is placed in each solution and the two are connected by a wire, electrons will flow from

the reducing solution to the oxidizing solution through the wire, and thus bring about the simultaneous reduction of the oxidizing agent and oxidation of the reducing agent, without ever having had them in contact with each other. Furthermore, the products thus obtained are the same as would have been formed if the original solutions had been mixed.

In this arrangement each container with its electrode is called a half-cell and the reaction taking place in the cell is called a half-cell or electron reaction. To illustrate, suppose a strip of copper is placed in a solution of copper sulfate and a strip of zinc in a solution of zinc sulfate. If these solutions are connected by a salt bridge and the metal strips are joined by a wire, electrons will flow through the wire from the zinc to the copper. Zinc will go into solution, and copper will be plated out. Each atom of zinc going into solution loses two electrons to become Zn^{++} ; that is, the zinc is oxidized. Likewise each copper ion that is discharged must gain two electrons; the copper is reduced. The half-cell or electron equations are



and the complete oxidation-reduction equation obtained by adding the two electron equations is



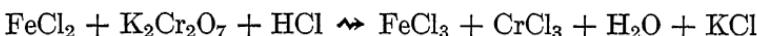
This is a very simple and familiar example. Additional examples are given in the discussion on the balancing of oxidation-reduction equations.

The Writing and Balancing of Redox Equations. *Redox* equations are often the cause of such great difficulty that many students try to evade the issue by attempting to memorize such equations as are encountered in the schemes of analysis. Aside from its possible value as a memory exercise, this method of attack is to be condemned, because it is so inefficient and unnecessary. A little mental effort devoted to understanding the ideas involved in writing these equations and to learning a systematic method of balancing them will enable one to handle any equation ordinarily encountered in analytical chemistry.

The fundamental fact upon which all systematic methods of balancing are based is that oxidation and reduction always take place in equivalent amounts; that is, exactly the same number

of electrons is lost by the reducing agent as is gained by the oxidizing agent. Any scheme for evaluating the number of electrons transferred therefore constitutes a method of balancing such equations. We shall consider two of the methods that may be employed for accomplishing this: the ion-electron method and the valence-electron method.

Example 1. Let us take as an example the oxidation of a solution of FeCl_2 by a solution of potassium dichromate acidified with HCl. Expressed in molecular form, the unbalanced equation is



We know that the ferrous ion here is oxidized to the ferric ion, whereas the dichromate ion is reduced to the chromic ion; since H^+ ions and the oxygens from the Cr_2O_7^- ion also are involved, water will be formed in the reaction. The unbalanced equation in ionic form can now be set down:



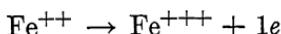
The components in this equation are now resolved into their two separate equations, that for the oxidation of Fe^{++} ion being



and for the reduction of the dichromate ion,



The number of electrons associated with each equation now must be assigned. It is simple to see that the oxidation of a ferrous ion to the ferric ion is the result of the former having lost a single electron, whether we arrive at this decision by saying that the net charge of 2 positive charges on the Fe^{++} ion are now 3 positive charges on the Fe^{+++} ion or whether we say that the electrovalence has been changed from +2 to +3, since in this case the valence states are indicated by the number of charges carried by iron. The half-cell or electron equation therefore is



The balancing of the electron equation for the reduction of the dichromate ion is not quite so simple. The way in which one determines the number of electrons which are transferred to the

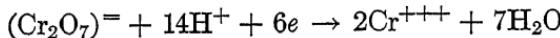
dichromate ion distinguishes the ion-electron method from the valence-electron method. To balance the electron equation,



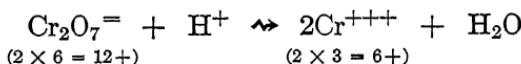
by the *ion-electron method*, the rule is first to balance chemically, that is, with respect to the number of atoms of each element involved. Since there are 2 chromium and 7 oxygen atoms in the Cr_2O_7^- radical, the reaction calls for 14H^+ giving 2 chromic ions (2Cr^{+++}) and $7\text{H}_2\text{O}$:



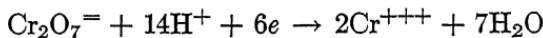
The equation next is balanced electrically; that is, the number of electrons required is ascertained. The $(\text{Cr}_2\text{O}_7)^-$ ion, as a whole, has 2 negative charges; the 14H^+ ions have a total of 14 positive charges, giving a net charge on the left side of the equation of $12+$. On the right side of the equation there are 2 chromic ions, each with 3 positive charges, or a total of $6+$. In order to have this electron equation, as a whole, electrically neutral, 6 negative charges, that is, 6 electrons, must be supplied. The balanced electron equation therefore is



The balancing of the electron equation for the reduction of the dichromate ion, by the *valence-electron* method, is based on determining the number of electrons needed, by the apparent change in valence undergone by the chromium atom. In $\text{K}_2\text{Cr}_2\text{O}_7$ or in the ion, Cr_2O_7^- , the "apparent valence" of each chromium atom is $+6$; we say that chromium here has an oxidation number of $+6$. This is deduced from the fact that each oxygen atom has a valence of -2 , and each potassium atom a valence of $+1$, which leaves $+12$ for both chromium atoms or $+6$ per atom of chromium. In the chromic ion, Cr^{+++} , the chromium has a valence of $+3$. We have, therefore, in the partly completed equation,

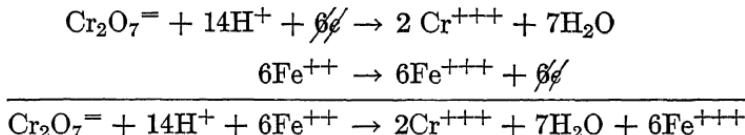


2 chromium atoms each suffering a valence decrease of $+3$ or a total of $+6$. This calls for 6 electrons. The 7 oxygen atoms require 14 hydrogen ions, forming $7\text{H}_2\text{O}$. The completed electron equation now can be written



These 6 electrons are furnished by the ferrous ions, and, since each Fe^{++} ion loses 1 electron, there are required 6 Fe^{++} ions to effect the reduction of the dichromate ion.

The two electron equations are then finally added:

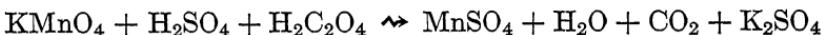


canceling the electrons which are transferred and giving the final complete equation in ionic form.

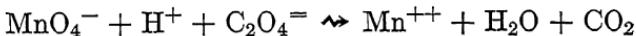
To transform the ionic equation into a molecular one, the non-essential ions easily can be inserted by inspection and associated with their proper partners in the form of molecules. In the equation just written the ions not included are 2K^+ from the $\text{K}_2\text{Cr}_2\text{O}_7$, 14Cl^- from 14HCl and 12Cl^- from 6FeCl_2 . These are paired off to give 2CrCl_3 , 6FeCl_3 and 2KCl . The balanced equation in molecular form is therefore



Example 2. Another example of balancing *redox* equations will be helpful. If oxalic acid, $\text{H}_2\text{C}_2\text{O}_4$, a good reducing agent, is added to a solution of KMnO_4 acidified with dilute H_2SO_4 , reduction of the permanganate takes place, with liberation of CO_2 . The reaction may be expressed, in molecular form, by the following unbalanced equation:



Rewriting this in ionic form to show only the ions and molecules actually concerned in the reaction, we have



The equations for the oxidizing agent and for the reducing agent are set up next. The MnO_4^- ion requires the presence of H^+ ions for its reduction to Mn^{++} . Accordingly, the components are assembled for this equation:



By the *ion-electron* method, the chemical balance requires 8H^+ for the 4 oxygen atoms in the MnO_4^- , giving $4\text{H}_2\text{O}$:



The electric charges are now 8+ on the hydrogen ions and -1 on the MnO_4^- ion, or a total of 7+ on the left side of the equation; only 2 positive charges remain on the manganeseous ion, the water being, of course, electrically neutral. To equalize the charges on both sides of the equation 5 electrons are required:



The balancing of this electron equation also might be done by the *valence-electron* method. In KMnO_4 or in the MnO_4^- ion, the manganese has an apparent valence or oxidation number of +7, but in Mn^{++} it is +2. There is a decrease of 5 positive charges requiring 5 electrons. As before, the chemical balance of atoms requires 8 hydrogen ions for the 4 oxygens, yielding $4\text{H}_2\text{O}$. The balanced electron equation is then as given in equation 1.

The reducing ion, C_2O_4^- , is oxidized to CO_2 . The equation for this change is easily balanced chemically:

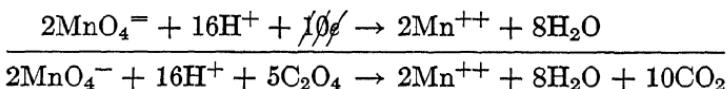
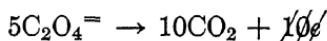


and, if the ion-electron method is used, since 2 negative charges are associated with the C_2O_4^- ion, and the oxidation product, CO_2 , is electrically neutral, 2 electrons are lost, and the balanced electron equation results:

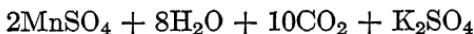


One might also balance this equation by the valence-electron method, but not so simply. In the formula $\text{H}_2\text{C}_2\text{O}_4$, each carbon atom has an average apparent valence of +3, since there are 4O- or 8- charges, offset by 2+ charges on the hydrogen atoms, giving +6 for both carbons or +3 for each carbon atom. In CO_2 each carbon has a valence of +4. There is thus an increase of apparent valence of +1 for each carbon atom or a total of +2, corresponding to the loss of 2 electrons.

To balance the electrons transferred from the reducing ion to the oxidizing ion, equation (2) must be multiplied by 5 and equation (1) by 2; when these are added together and the electron canceled, we have

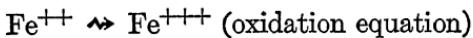
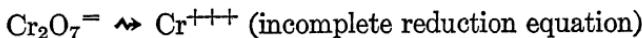


To restore this ionic equation to the original molecular equation, in order to show how many molecules of the two acids, H_2SO_4 and $\text{H}_2\text{C}_2\text{O}_4$, are required, it is merely necessary to assign 10H^+ to the $5\text{C}_2\text{O}_4^{=}$; the remaining 6H^+ are furnished by $3\text{H}_2\text{SO}_4$. The 2MnO_4^- ions correspond to 2KMnO_4 . Two $\text{SO}_4^{=}$ ions account for 2MnSO_4 , and 2K^+ with the remaining $\text{SO}_4^{=}$ are written as K_2SO_4 . It thus is found that 2 moles of KMnO_4 react with 5 moles of $\text{H}_2\text{C}_2\text{O}_4$, involving at the same time 3 moles of H_2SO_4 :



Rules for Balancing Redox Equations. 1. If the original unbalanced equation is presented in molecular form, the products being given, strip the equation of its non-essential or incidental ions, and rewrite the equation in ionic form. If the reagents which are brought together and the essential products of the reaction are stated or known, set down only the essential ions and products as an unbalanced ionic equation. It is necessary, of course, to know in any case what the reduction and oxidation products are.

2. The oxidizing agent and the product to which it is reduced then are picked out and set down as a partial skeleton equation; the same is done for the reducing agent and the product to which it is oxidized. For the first example selected:



This step, which necessitates the recognition of the oxidizing and reducing agents, is the most troublesome part of any method of handling *redox* equations. Suggestions are given later for making it easier, but there is no way of eliminating entirely the requirement of a background of specific chemical information in dealing with it.

3. Next, balance the equations chemically, so that there are the same number of atoms of each element on each side of the equation. No difficulty is encountered in those cases in which only one element in an ion is involved, but generally where oxy-ions are concerned, H^+ , OH^- or H_2O must be introduced. If it is known definitely that the reaction proceeds in an acid solution, H^+ ions are supplied to the left side of the equation, H_2O being one of the

products of the reaction; or, in an alkaline medium, OH^- ions appear as initial reactants. In the case illustrated the reduction equation becomes



4. Evaluate the electron gain or loss in each electron reaction by either the ion-electron method or the valence-electron method. In the ion-electron method, this is done by finding the algebraic sum of the charges on the ions on the right and subtracting it algebraically from the sum found similarly for the charges on the left (this is the distinctive feature of this method). It is absolutely necessary to have the proper charge attached to each ion before the electron transfer is evaluated. This evaluation can easily be carried out mentally.

By the valence-electron method determine the change of valence of the element concerned.

5. Multiply each equation by factors which will equalize the number of electrons lost by the reducing agent and gained by the oxidizing agent, and then add the two electron equations; this step cancels the electrons.

6. If it is desired to include the incidental ions, that is, to write the final balanced equation in molecular form, this may be done by adding to both sides of the balanced ionic equation a sufficient number of each incidental ion to put it in the form of the original (unbalanced) molecular equation.

Some Suggestions for Balancing Redox Equations. To aid in picking out oxidizing and reducing agents, the following hints may be useful, provided the complete unbalanced equation is available.

Ions of non-variable valence elements such as K^+ , Na^+ , Ca^{++} , Sr^{++} , Ba^{++} , Al^{+++} , are never involved in *redox* reactions and should be ignored. Be on the lookout for such ions and compounds as MnO_4^- , $\text{CrO}_4^=$ or $\text{Cr}_2\text{O}_7^=$, NO_2^- , Cl^- or Cl_2 , Br^- or Br_2 , I^- or I_2 , $\text{S}^=$ or H_2S , H_2O_2 , $\text{SO}_3^=$, Fe^{++} or Fe^{+++} , and the like. Other examples are listed in Tables VII and VIII. If any of these substances are present, they are almost certain to be involved in the reaction.

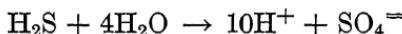
If an element is present in the elementary form on one side of the equation, it is likely to be involved. The electron equation

then is formed by the use of the free element and the ion which is present on the other side of the equation.

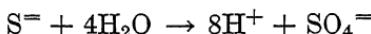
Many oxy-ions are either oxidizing or reducing agents, and some even may be reduced or oxidized to other oxy-ions of the same element.

If the products of the reaction are not known, only experimental evidence can supply them with certainty. For common oxidizing and reducing agents, however, the behavior is so well known that the products can be predicted correctly in almost all cases. Some information on which such a prediction may be based is given in the discussion of oxidizing and reducing agents.

If there is doubt as to whether or not a particular substance is ionized, no error will be introduced by using it in either the ionized or the non-ionized form. The oxidation of H_2S to $\text{SO}_4^=$, for example, may be formulated with equal accuracy either as



or else as



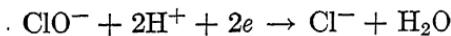
If a reaction is known to take place in basic solution, it is preferable to use OH^- ions and H_2O in balancing the electron equation. However, if it is not known that the reaction requires an alkaline environment and H^+ and H_2O are used in the balancing procedure, H^+ will appear among the products on the right in the balanced ionic equation. When this situation occurs, hydroxyl ions equal in number to the hydrogen ions are added to both sides of the equation. The H^+ and OH^- on the right then are combined into H_2O , and the appearance of OH^- on the left then indicates the necessity of a basic solution, when this was not known at the outset.

Sometimes two elements in the same compound are oxidized or reduced, as when As_2S_3 or Cu_2S is dissolved in HNO_3 . Such cases are handled easily by keeping the constituents in the stoichiometric relations indicated by the formula (2As to 3S; 2Cu to 1S) and proceeding with the balancing in the usual way.

Sometimes the same substance acts both as the oxidizing agent and as the reducing agent, that is, oxidizes and reduces itself. An example is the transformation of a hypochlorite into a chlorate and a chloride:



Such an equation is balanced by a direct application of the ion-electron method, the ion in question being used in both electron equations:



Then,



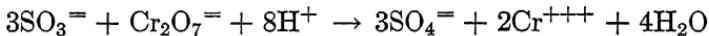
or



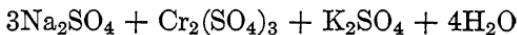
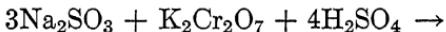
In the molecular form,



Sometimes a certain ion may be present in the unbalanced molecular equation both as an essential and as an incidental ion. This is frequently true of $\text{SO}_4^{=}$, Cl^- and NO_3^- . For example, if we compare the balanced ionic equation,



with the balanced molecular equation,



it will be noticed that, of the 7 $\text{SO}_4^{=}$ ions on the right in the latter equation, only 3 are included in the ionic equation. These 3 $\text{SO}_4^{=}$ ions are essential, whereas the other 4 $\text{SO}_4^{=}$ ions are purely incidental.

Oxidizing and Reducing Reagents. In considering what ions and substances can be oxidized or reduced or, conversely, what ions or other substances constitute reducing and oxidizing agents, it must be remembered, in the first place, that many of the cations and most of the anions, present in the test solutions and in known mixtures and in samples, have either oxidizing or reducing tendencies. For example, Sn^{++} , Fe^{++} , AsO_2^- , I^- , Br^- , $\text{SO}_3^{=}$, $\text{S}_2\text{O}_3^{=}$, $\text{S}^{=}$, $\text{C}_2\text{O}_4^{=}$ and CN^- are strong reducing ions; on the other hand, such ions as Fe^{+++} , $\text{AsO}_4^{=}$, $\text{Cr}_2\text{O}_7^{=}$ and MnO_4^- are strongly oxidizing. Ions of this kind become oxidized or reduced by the addition to the solution of oxidizing or reducing agents. In the second place, the addition of an oxidizing or a reducing reagent may be either

for the express purpose of causing a desired oxidation or reduction or for some other reason, the accompanying oxidation or reduction being merely an incidental effect. For example, stannous chloride is utilized as a reducing agent in the test for mercury; bromine sometimes is employed to oxidize iron to the ferric condition, and KMnO_4 to oxidize the oxalate ion. But H_2S , for example, used as a precipitating agent, also will act as a reducing agent toward any oxidizing ions present in the solution. HNO_3 , if used as a solvent, will function also as an oxidizing agent; in fact, its effective solvent action is attributable to its strong oxidizing tendency.

The more important and frequently used reagents which have oxidizing ability are listed in Table VII. The table gives the form

TABLE VII
COMMON OXIDIZING AGENTS

Reagent	Electron Reaction	Change in Apparent Valence per Atom of Element Involved
I_2	$\text{I}_2 + 2e \rightleftharpoons 2\text{I}^-$	$0 \rightarrow -1$
Br_2	$\text{Br}_2 + 2e \rightleftharpoons 2\text{Br}^-$	$0 \rightarrow -1$
Cl_2	$\text{Cl}_2 + 2e \rightleftharpoons 2\text{Cl}^-$	$0 \rightarrow -1$
KClO_3	$\text{ClO}_3^- + 6\text{H}^+ + 6e \rightleftharpoons \text{Cl}^- + 3\text{H}_2\text{O}$	$0 \rightarrow -1$
NaClO	$\text{ClO}^- + 2\text{H}^+ + 2e \rightleftharpoons 2\text{Cl}^- + \text{H}_2\text{O}$	$+1 \rightarrow -1$
HNO_3 (dilute)	$\text{NO}_3^- + 4\text{H}^+ + 3e \rightleftharpoons \text{NO} + 2\text{H}_2\text{O}$	$+5 \rightarrow +2$
HNO_3 (conc.)	$\text{NO}_3^- + 2\text{H}^+ + 1e \rightleftharpoons \text{NO}_2 + \text{H}_2\text{O}$	$+5 \rightarrow +4$
Aqua regia	$\text{NO}_3^- + 4\text{H}^+ + 3e \rightleftharpoons \text{NO} + 2\text{H}_2\text{O}$	$+5 \rightarrow +2$
Na_2O_2	$\text{Na}_2\text{O}_2 + 2\text{H}_2\text{O} + 2e \rightleftharpoons 2\text{Na}^+ + 4\text{OH}^-$	$0 \rightarrow -2$
H_2O_2	$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2e \rightleftharpoons 2\text{H}_2\text{O}$	$0 \rightarrow -2$
NaBiO_3	$\text{BiO}_3^- + 6\text{H}^+ + 2e \rightleftharpoons \text{Bi}^{+++} + 3\text{H}_2\text{O}$	$+5 \rightarrow +3$
$\text{K}_2\text{Cr}_2\text{O}_7$	$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6e \rightleftharpoons 2\text{Cr}^{+++} + 7\text{H}_2\text{O}$	$+6 \rightarrow +3$
KMnO_4 (acid)	$\text{MnO}_4^- + 8\text{H}^+ + 5e \rightleftharpoons \text{Mn}^{++} + 4\text{H}_2\text{O}$	$+7 \rightarrow +2$
KMnO_4 (basic)	$\text{MnO}_4^- + 4\text{H}^+ + 3e \rightleftharpoons \text{MnO}_2 + 2\text{H}_2\text{O}$	$+7 \rightarrow +4$

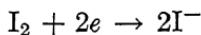
in which the reagent is supplied, the element or ion responsible for the oxidation, its reduction product and the apparent valence of the element in its oxidized and reduced form, together with the number of electrons gained per ion. Reducing reagents are tabulated in Table VIII in the same way.

Some comment on these reagents should be helpful in balancing *redox* equations involving these substances. The important matter to bear in mind is the writing and balancing of the electron reactions concerned.

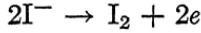
TABLE VIII
COMMON REDUCING AGENTS

<i>Reagent</i>	<i>Electron Reaction</i>	<i>Change in Apparent Valence per Atom of Element Involved</i>
FeSO ₄	Fe ⁺⁺ \rightleftharpoons Fe ⁺⁺⁺ + 1e	+2 \rightarrow +3
SnCl ₂	Sn ⁺⁺ \rightleftharpoons Sn ⁺⁺⁺⁺ + 2e	+2 \rightarrow +4
NH ₄ I	2I ⁻ \rightleftharpoons I ₂ + 2e	-1 \rightarrow 0
Na ₂ SO ₃	SO ₃ ⁼ + H ₂ O \rightleftharpoons SO ₄ ⁼ + 2H ⁼ + 2e	+4 \rightarrow +6
H ₂ S	S ⁼ \rightleftharpoons S° + 2e	-2 \rightarrow 0
H ₂ S	S ⁼ + 4H ₂ O \rightleftharpoons SO ₄ ⁼ + 8H ⁺ + 8e	-2 \rightarrow +6
H ₂ C ₂ O ₄	C ₂ O ₄ ⁼ \rightleftharpoons 2CO ₂ + 2e	+3 \rightarrow +4
NaAsO ₂	AsO ₂ ⁻ + 2H ₂ O \rightleftharpoons AsO ₄ ⁼ + 4H ⁺ + 2e	+3 \rightarrow +4
Na ₂ S ₂ O ₃	2S ₂ O ₃ ⁼ \rightleftharpoons S ₄ O ₆ ⁼ + 2e	+2 \rightarrow +2½
H ₂ O ₂	H ₂ O ₂ \rightleftharpoons O ₂ + 2H ⁺ + 2e	-2 \rightarrow 0
Hydrogen	H ₂ \rightleftharpoons 2H ⁺ + 2e	0 \rightarrow +1
Metals, e.g. Zn	Zn° \rightleftharpoons Zn ⁺⁺ + 2e	0 \rightarrow +2

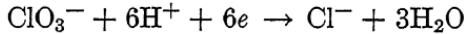
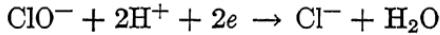
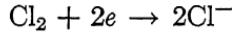
The Halogens. In the form of the free element Cl₂, Br₂ and I₂ are oxidizing agents and are reduced to the simple anion form. For example, the change for iodine is



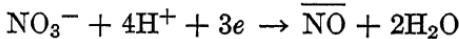
The iodide ion, I⁻, and the bromide ion, Br⁻, are reducing agents. The former frequently is supplied in analytical procedures in the form of NH₄I or KI:



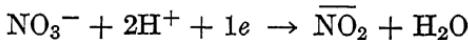
Free chlorine, NaClO and KClO₃, are all oxidizing substances which are reduced to Cl⁻ ion. The electron equations are



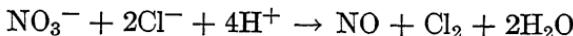
Nitric Acid. This oxidizing solvent frequently is used in dissolving sulfides and metals. When the acid is dilute, the NO₃⁻ ion is reduced to NO:



If the acid is concentrated, the reduction product is NO₂:



Aqua Regia. This is a mixture of concentrated HNO_3 and concentrated HCl . The solution contains NO_3^- , Cl^- and H^+ ions and owes its oxidizing ability to NO_3^- which is reduced, as in nitric acid, to NO . When this reagent decomposes, according to the reaction,

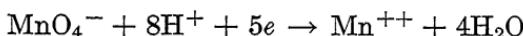


the free chlorine which is liberated may exert a strong oxidizing effect and thus account for the strong oxidizing action of this reagent.

Potassium Permanganate. This very strong oxidizer may be reduced, by a reducing agent, either to hydrated MnO_2 or else to Mn^{++} . The former reaction takes place in an alkaline or neutral solution, according to the half-cell equation:

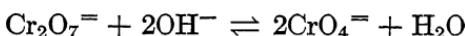


In an acidic medium, the reaction (already given on page 102) is

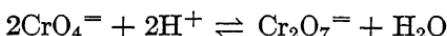


This is a case where the product of the reduction is determined by the acidity or alkalinity of the medium.

Chromates and Dichromates. A somewhat similar situation exists in the case of the chromates and dichromates, the difference being that here it is the formula of the reactant and not that of the product which is determined by the acid or basic nature of the medium. The form of the ion present is dependent solely upon the acidity of the solution, as can be seen from the equations:



and



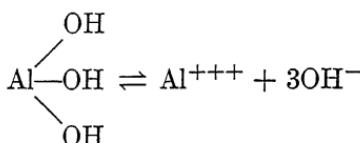
Hence, in alkaline solution the chromate ion predominates; in acid solution the dichromate ion predominates.

THE THEORY OF AMPHOTERISM

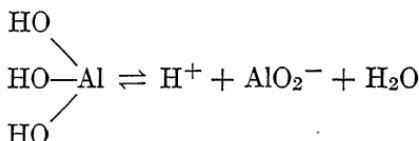
An amphoteric or amphiprotic compound is one which has the properties of both an acid and a base. Many oxides and hydroxides and some sulfides are amphoteric and react both as acids and as bases. This is especially true of the hydroxides of the elements occupying positions near the middle of the periodic table. Of

special interest to us are the hydroxides of aluminum, chromium, zinc, antimony and tin.

Aluminum hydroxide will be taken here as a typical example to illustrate the behavior of amphoteric hydroxides. The ionization of $\text{Al}(\text{OH})_3$ as a base can be represented thus:



and as an acid:



yielding H^+ ion from its primary ionization, the meta-aluminate ion, AlO_2^- , and H_2O . In an aqueous solution of aluminum hydroxide (a very dilute one, since $\text{Al}(\text{OH})_3$ is very sparingly soluble in water) there exist aluminum and hydroxyl ions in equilibrium with hydrogen and meta-aluminate ions. On the basis of this double equilibrium, we can see why $\text{Al}(\text{OH})_3$ will dissolve on the one hand, in acids to form aluminum salts and, on the other hand, in bases to form aluminates. In the first case, the hydroxyl ions coming from the ionization of $\text{Al}(\text{OH})_3$ are used up by the hydrogen ions from the acid, and this results in more solid being dissolved to restore equilibrium; the comparatively high hydrogen-ion concentration forces back the ionization of $\text{Al}(\text{OH})_3$ as an acid. In the second case when an alkali such as NaOH is added to $\text{Al}(\text{OH})_3$, the hydrogen-ion concentration is lowered by neutralization, and, at the same time, the ionization of $\text{Al}(\text{OH})_3$ as a base is repressed; to restore equilibrium again, more solid must dissolve and ionize. Thus in either case final equilibrium is established when all the solid has dissolved.

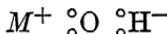
The tendency for $\text{Al}(\text{OH})_3$ to ionize as a base is somewhat more marked than its tendency to ionize as an acid; in other words, a saturated solution of aluminum hydroxide contains more hydroxyl ions than hydrogen ions. With $\text{Zn}(\text{OH})_2$ the basic tendency is still more marked; with certain other amphoteric hydroxides such as H_3AsO_3 the acid tendency predominates.

The Electronic Explanation of Amphotericism. A hydroxide, MOH , where M may be a single element or a radical, has two possible modes of ionization: it may form M^+ and OH^- or H^+ and MO^- ions. The form that predominates is determined by the tendency of M to attract or give up electrons. This can be made clear in the following way.

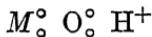
The molecule MOH is held together by 2 electron-pair bonds. Suppose first of all that M is H or some group which has the same attraction for electrons as H. The 2 pairs of electrons then will be shared approximately equally; that is, they will be the same distance from the O atom:



Next, if M is some element or group which has a very slight attraction for electrons, the electron pair on the left will be displaced toward the oxygen, and, if the displacement is sufficient, an ionic bond is formed between M and O; that is, the compound consists of the ion M^+ and OH^- . It may be noted that, since the O atom has but a limited ability to attract and hold electrons, if the pair on the left is moved closer to the O, the pair on the right must move farther away, that is, closer to the H; this latter effect corresponds to a decrease in the tendency to liberate a hydrogen ion, which may be one reason why we do not observe ionization into M^+ , H^+ , and O^- ions. The following diagram illustrates the situation:



The remaining possibility is that M may be some element or group which has a very strong attraction for electrons. In this case the electron pair on the left will be displaced toward M , and that on the right toward O or away from H:



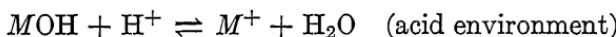
If this effect is sufficiently pronounced, it means that the compound is ionized into H^+ and MO^- ions.

Since the OH^- ion is a base, we may refer to ionization according to the first scheme as ionization as a base and ionization according to the second scheme as ionization as an acid.

The elements in groups I and II of the periodic table have a pronounced tendency to give up electrons, and therefore their hydroxides are ionized as bases; these elements form the strong alkali hydroxides, such as $NaOH$ and KOH . Similarly, the ele-

ments of groups VI and VII of the periodic table have a considerable tendency to attract electrons. Therefore, if M is a radical containing an element of these groups, the hydroxide will be ionized as an acid; these elements form the strong oxygen acids, such as $\text{SO}_2(\text{OH})_2$ or H_2SO_4 and ClO_3OH or HClO_4 .

But what of the elements of groups III, IV and V? Most of these elements have no decided tendency either to repel or to attract electrons and therefore rarely, if ever, form simple ions. The hydroxides of most of these elements, as would be expected, show no decided tendency to ionize either as acids or as bases and, in fact, show both kinds of ionization simultaneously. If such hydroxides are in an acid environment, the OH^- will be removed by combination with H^+ , and the ionization as a base will be favored; similarly, in an alkaline environment, the ionization as an acid is favored:



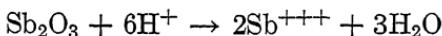
Amphotерism is shown especially by the hydroxides of the elements of groups III, IV and V of the periodic table; the hydroxides of N and P, however, are decidedly more acidic than basic in character. The most decidedly amphoteric elements are found near a line drawn diagonally from the upper left-hand to the lower right-hand corner of the conventional periodic table; elements such as N and P which are not relatively near this line are not likely to be appreciably amphoteric, even though they may be in groups III, IV and V.

As we go from top to bottom in a main group of the periodic table, the size of the atoms increases, and so the ability of the nucleus to hold electrons in the outermost orbit decreases; the ability to attract extra electrons to this orbit also decreases. This means that, for any main group, the basicity of the hydroxides will increase or—to say the same thing in another way—the acidity of the hydroxides will decrease in going from top to bottom in the table. Hence, in regard to the groups at the left in the table, the tendency to be amphoteric will be greatest for the elements at the top of the groups; at the right the tendency will be greatest for the elements at the bottom.

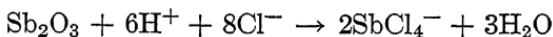
It must not be supposed that the hydroxides are the only compounds that exhibit amphoterism. As is to be expected from the

analogous behavior of sulfur and oxygen compounds, the sulfides of many metals are also amphoteric. We can illustrate the similarity in the following way:

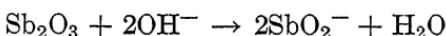
Antimony oxide is a typical amphoteric compound. This oxide is soluble in either strongly acid or alkaline solutions:



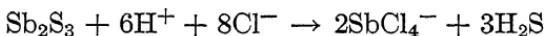
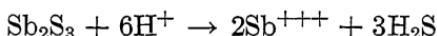
or



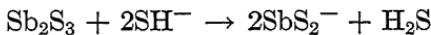
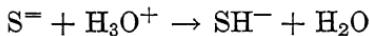
and



The sulfide is likewise soluble in either acid or alkaline solution:



If, instead of an alkali hydroxide, an alkali sulfide, such as Na_2S , is used, solution of Sb_2S_3 takes place in much the same way:



The amphoteric nature of hydroxides and sulfides is utilized in qualitative analysis to effect a number of separations. Of particular importance is the separation of the group II sulfides into two divisions and the separation of aluminum and chromium from iron and manganese, and zinc from nickel and cobalt in group III.

It is possible to set up equilibrium expressions for reactions involving amphoteric behavior but, because of such factors as the indefiniteness of the formulas of many amphoteric substances, quantitative calculations are practically, if not entirely, meaningless.

QUESTIONS AND PROBLEMS—SET 4. REDOX EQUATION WRITING

1. Define and illustrate: electrovalence; oxidation; reduction; "half-cell" or electron reaction.

2. Find the apparent valence of the indicated element in each of the following compounds:

(a) S in Na_2SO_4 , Na_2SO_3 , $\text{Na}_2\text{S}_2\text{O}_3$, Na_2S , SO_2

(b) Cr in CrCl_2 , CrCl_3 , CrO_2Cl_2 , K_2CrO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$

(c) N in NH_3 , HNO_2 , HNO_3 , BiONO_3 , N_2O , NO
 (d) Mn in MnSO_4 , HMnO_4 , K_2MnO_4 , $\text{MnO}(\text{OH})_2$, MnO_2

3. Name 5 elements, exclusive of Fe, Mn, Cr, As and N, which exhibit variable valence, and write the corresponding balanced electron equations for each. Why do we not have oxidation or reduction taking place with elements such as Na, Ca, Al and Zn (other than reduction to the metallic state)?

4. Complete and balance the following electron equations, using the ion-electron method:

(a) $\text{MnO}_4^- + \text{H}^+ + e \rightsquigarrow \text{Mn}^{++} + \text{H}_2\text{O}$
 (b) $\text{Cr}_2\text{O}_7^- + \text{H}^+ + e \rightsquigarrow \text{Cr}^{+++} + \text{H}_2\text{O}$
 (c) $\text{AsO}_4^{= \equiv} + \text{H}^+ + e \rightsquigarrow \text{AsO}_2^- + \text{H}_2\text{O}$
 (d) $\text{NO}_3^- + \text{H}^+ + e \rightsquigarrow \text{NO} + \text{H}_2\text{O}$

5. Show how the electron equations of question 4 are balanced by the valence-electron method.

6. Balance the following equations:

(a) $\text{Cr}_2\text{O}_7^- + \text{I}^- + \text{H}^+ \rightsquigarrow \text{Cr}^{+++} + \text{I}_2 + \text{H}_2\text{O}$
 (b) $\text{MnO}_4^- + \text{I}^- + \text{H}^+ \rightsquigarrow \text{Mn}^{++} + \text{I}_2 + \text{H}_2\text{O}$
 (c) $\text{AsO}_4^{= \equiv} + \text{I}^- + \text{H}^+ \rightsquigarrow \text{AsO}_2^- + \text{I}_2 + \text{H}_2\text{O}$
 (d) $\text{NO}_3^- + \text{S}^- + \text{H}^+ \rightsquigarrow \text{NO} + \text{S}^\circ + \text{H}_2\text{O}$

7. Balance the following equations:

(a) $\text{Bi}^{+++} + \text{SnO}_2^- + \text{OH}^- \rightsquigarrow \text{Bi}^\circ + \text{SnO}_3^- + \text{H}_2\text{O}$
 (b) $\text{MnO}_4^- + \text{S}^- + \text{H}^+ \rightsquigarrow \text{Mn}^{++} + \text{S}^\circ + \text{H}_2\text{O}$
 (c) $\text{PbO}_2 + \text{Mn}^{++} + \text{H}^+ \rightsquigarrow \text{Pb}^{++} + \text{MnO}_4^- + \text{H}_2\text{O}$
 (d) $\text{Cr}_2\text{O}_7^- + \text{NO}_2^- + \text{H}^+ \rightsquigarrow \text{Cr}^{+++} + \text{NO}_3^- + \text{H}_2\text{O}$

8. Balance the following equations:

(a) $\text{HgCl}_2 + \text{SnCl}_2 \rightsquigarrow \text{Hg}_2\text{Cl}_2 + \text{SnCl}_4$
 (b) $\text{KMnO}_4 + \text{H}_2\text{SO}_3 \rightsquigarrow \text{H}_2\text{SO}_4 + \text{MnSO}_4 + \text{K}_2\text{SO}_4 + \text{H}_2\text{O}$
 (c) $\text{HNO}_3 + \text{Bi}_2\text{S}_3 \rightsquigarrow \text{Bi}(\text{NO}_3)_3 + \text{S}^\circ + \text{NO} + \text{H}_2\text{O}$
 (d) $\text{KI} + \text{Cl}_2 \rightsquigarrow \text{I}_2 + \text{KCl}$

9. Balance the following equations:

(a) $\text{I}_2 + \text{H}_2\text{S} \rightsquigarrow \text{S} + \text{HI}$
 (b) $\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{S} + \text{HCl} \rightsquigarrow \text{CrCl}_3 + \text{KCl} + \text{S}^\circ + \text{H}_2\text{O}$
 (c) $\text{KMnO}_4 + \text{H}_2\text{C}_2\text{O}_4 + \text{H}_2\text{SO}_4 \rightsquigarrow \text{MnSO}_4 + \text{K}_2\text{SO}_4 + \text{CO}_2 + \text{H}_2\text{O}$
 (d) $\text{Na}_2\text{O}_2 + \text{Fe}(\text{OH})_2 + \text{H}_2\text{O} \rightsquigarrow \text{Fe}(\text{OH})_3 + \text{NaOH}$

10. Balance the following equations:

(a) $\text{PbS} + \text{HNO}_3 \rightsquigarrow \text{PbSO}_4 + \text{NO} + \text{H}_2\text{O}$
 (b) $\text{HgS} + \text{HNO}_3 + \text{HCl} \rightsquigarrow \text{HgCl}_2 + \text{S}^\circ + \text{NO} + \text{H}_2\text{O}$
 (c) $\text{Na}_2\text{O}_2 + \text{Mn}(\text{OH})_2 + \text{H}_2\text{O} \rightsquigarrow \text{MnO}(\text{OH})_2 + \text{NaOH}$
 (d) $\text{Sb}_2\text{S}_5 + \text{HCl} \rightsquigarrow \text{SbCl}_3 + \text{S}^\circ + \text{H}_2\text{S}$

THE METALS OF THE AMMONIUM HYDROXIDE SUBGROUP: IRON
(Fe^{++} , Fe^{+++}), ALUMINUM (Al^{+++}), MANGANESE (Mn^{++}),
CHROMIUM (Cr^{+++})

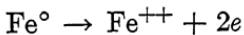
IRON, Fe^{++} , Fe^{+++}

Iron is the second most abundant metal and fourth most abundant element in the earth's crust, the amount being approximately 5 per cent. The commercially important ores are hematite, Fe_2O_3 ; magnetite, Fe_3O_4 ; limonite, $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$; and siderite, FeCO_3 . These ores are reduced to metallic iron in the blast furnace.

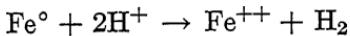
Aside from the uses of the metal in the form of cast and wrought iron and steel, iron has important applications as a pigment in red paints (Fe_2O_3), in laundry bluing, blueprints and blue-black inks. Iron is present as the catalyst in the Haber method of synthesizing ammonia and in other industrial processes. The hemoglobin in the blood is an iron compound, and many medicinal preparations contain this element.

Iron forms two series of compounds, namely, (1) ferrous, in which the iron is divalent, and (2) ferric, in which the iron is trivalent.

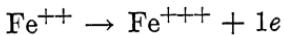
Ferrous Ion, Fe^{++} . This ion is formed when an atom of iron loses two electrons:



This may be brought about, as, for instance, when iron is dissolved in a non-oxidizing acid such as HCl:



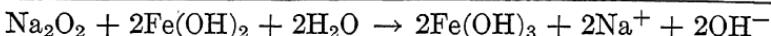
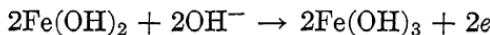
The ferrous ion is easily oxidized to the trivalent ferric form through the loss of one electron:



The oxidizing agent may be the oxygen of the atmosphere or some other oxidizing agent, such as HNO_3 , KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, Na_2O_2 or Br_2 . See the *redox* equations discussed in the preceding section.

Sodium peroxide, Na_2O_2 , is used in the procedure of analysis to oxidize iron (as well as manganese and chromium). This is one of the few oxidizing agents which is employed in an alkaline medium.

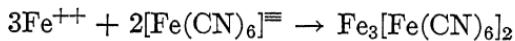
The equation for this reaction is balanced by the ion-electron method in the following manner:



In a natural but not in an acid solution H_2S precipitates black FeS . If the solution is first made alkaline, greenish-white Fe(OH)_2 precipitates. Since, however, FeS is less soluble than Fe(OH)_2 , the precipitate is transformed into FeS when H_2S is passed into the solution.

The Fe^{++} ion forms a complex cyanide ion, the ferrocyanide ion, $[\text{Fe}(\text{CN})_6]^{4-}$. This reacts with Fe^{+++} ion to produce Prussian blue (see test for ferric iron, page 118).

Potassium ferricyanide, $\text{K}_3\text{Fe}(\text{CN})_6$, produces with Fe^{++} ions a blue precipitate of ferrous ferricyanide known as Turnbull's blue:

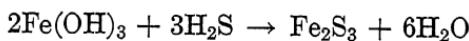


This is the usual test for ferrous ion.

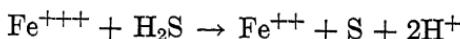
Ferrous salts, such as FeSO_4 , are strong reducing agents because the ferrous ion is so easily oxidized to the ferric state. They are employed extensively for this purpose in analytical chemistry.

Ferric Ion, Fe^{+++} . Sodium or ammonium hydroxide produces a red-brown precipitate of the hydroxide or hydrated oxide, inappreciably soluble in excess; this means that ferric hydroxide is not amphoteric. The formula of the precipitate usually is written Fe(OH)_3 though it is probably a hydrated oxide, such as $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$.

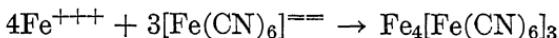
Addition of an alkali sulfide such as $(\text{NH}_4)_2\text{S}$ to a solution containing Fe^{+++} ion causes the precipitation of black Fe_2S_3 . If H_2S is passed into an alkaline solution containing precipitated Fe(OH)_3 , the hydroxide is changed into the sulfide:



In acid solutions the Fe^{+++} ion oxidizes H_2S with the formation of free sulfur, and no sulfide precipitate is obtained:



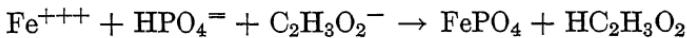
Potassium ferrocyanide, $K_4Fe(CN)_6$, produces with the Fe^{+++} ion a deep-blue precipitate of ferric ferrocyanide:



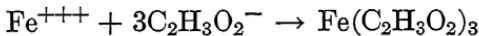
This is known as Prussian blue and is the usual test for ferric iron.

Potassium thiocyanate, $KSCN$ or other soluble thiocyanates form with the ferric ion a blood-red complex ion of the probable composition $[Fe(SCN)_6]^{---}$. This is one of the most sensitive reactions of the ferric ion. Other ions that form complex ions with Fe^{+++} ion, such as the phosphate, acetate, oxalate and other organic ions, decrease the intensity of the color.

Phosphates in ammoniacal, neutral or slightly acid solutions precipitate Fe^{+++} ion as ferric phosphate, $FePO_4$. If $NaC_2H_3O_2$ or $NH_4C_2H_3O_2$ is added, the precipitation of the phosphate is complete:



If phosphates are present in mixtures being analyzed and are not removed, a part of the group III precipitate will consist of $FePO_4$. This reaction is involved in the systematic procedure of analysis when interfering phosphates are present (see Part III, page 342). Acetates, when added in excess to an acetic acid solution of ferric iron, turn the solution red because of the formation of non-ionized ferric acetate:



This reaction also is utilized in the phosphate removal discussed in Part III. Ferric acetate reacts in dilute solution upon boiling, and forms basic ferric acetate, $Fe(OH)_2C_2H_3O_2$. This reaction frequently is used in analytical chemistry.

PRELIMINARY EXPERIMENTS

1. Action of Group Reagent on Ferric Solutions. To 2 drops of ferric nitrate, $Fe(NO_3)_3$, test solution add dilute NH_4OH . Observe the nature of the precipitate formed. Write the equation.

Add an excess of the reagent and shake. Add some NH_4Cl to the $Fe(OH)_3$, warm and shake. Does the precipitate dissolve in either case? Does Fe^{+++} ion form a complex with NH_3 ?

2. Action of $NaOH$ and Na_2O_2 . (a) Dissolve a few crystals of $FeSO_4$ in a milliliter of water. To a drop of this solution add dilute $NaOH$ until the solution is strongly alkaline. What is the precipitate which forms? Is it soluble in excess of $NaOH$? Is $Fe(OH)_2$ amphoteric?

(b) Add a little sodium peroxide to the Fe(OH)_2 . What happens? Write the equation whereby the compound is oxidized. Determine whether the product which forms is soluble in an excess of NaOH . Keep this result in mind when similar experiments are performed with Al(OH)_3 , Cr(OH)_3 and Zn(OH)_2 . Is Fe(OH)_3 amphoteric?

3. Prussian Blue Test for Ferric Iron. Centrifuge the ferric hydroxide obtained in experiment 2, dissolve it in dilute HCl , and to a part of the solution add a few drops of potassium ferrocyanide, $\text{K}_4\text{Fe}(\text{CN})_6$, reagent. Name the product and write the equation.

Repeat the experiment, using potassium ferricyanide, $\text{K}_3\text{Fe}(\text{CN})_6$, instead of the ferrocyanide. Note the result.

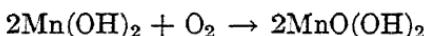
4. Thiocyanate Test for Ferric Iron. To a drop of the ferric test solution add a drop of potassium or ammonium thiocyanate, KSCN or NH_4SCN , reagent or a small crystal of the solid salt. Note the result. Write the equation for the reaction. This is an extremely sensitive test for ferric iron.

MANGANESE, Mn^{++}

Manganese is present in many iron ores, but the principal source is pyrolusite, MnO_2 . The pure metal is almost never prepared commercially; instead, alloys of iron and manganese, such as ferromanganese containing about 75 per cent Mn, or spiegeleisen (5-30 per cent Mn), are made. These are suitable for adding manganese to steel, the principal use of the metal, for the purpose of purifying it or for the making of special manganese-alloy steels. Pyrolusite is used in glass and in ceramic glazes, as the depolarizer in dry cells and as a drying agent in black paints.

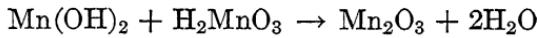
The compounds of manganese of importance from an analytical standpoint are the divalent manganous salts such as $\text{Mn}(\text{NO}_3)_2$, $\text{Mn}(\text{OH})_2$, MnS ; the tetravalent compounds of which MnO_2 and $\text{MnO}(\text{OH})_2$ are typical; manganates such as Na_2MnO_4 in which this element has an apparent valence of + 6; and the permanganates, especially KMnO_4 , in which manganese has an apparent valence of + 7 in the MnO_4^- anion.

Manganous hydroxide is formed when a manganous salt is treated with NaOH or NH_4OH . The product of the reaction, $\text{Mn}(\text{OH})_2$, white when first formed, rapidly changes through partial oxidation to a brown basic oxide whose composition may be represented by the formula $\text{MnO}(\text{OH})_2$:



This product also may be considered to be hydrated manganese dioxide, $\text{MnO}_2\text{H}_2\text{O}$; or, when written H_2MnO_3 , it may be called

manganous acid. As manganous acid it may react further with $\text{Mn}(\text{OH})_2$ to produce Mn_2O_3 :



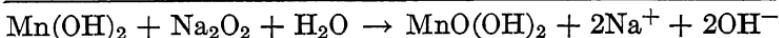
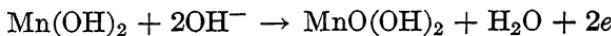
This latter product is, in fact, manganous manganite, MnMnO_3 , that is, the manganese salt of manganous acid.

The hydroxide is insoluble in an excess of NH_4OH or added NH_4Cl . In this respect, manganese differs from nickel, cobalt and zinc; it does not form a complex ion with ammonia.

In an excess of NaOH , $\text{Mn}(\text{OH})_2$ is insoluble. This means that it is not amphoteric in the sense that $\text{Al}(\text{OH})_3$, $\text{Cr}(\text{OH})_3$ and $\text{Zn}(\text{OH})_2$ are. This difference in behavior serves to separate manganese and iron from aluminum and chromium and is the method of separation used in the systematic procedure.

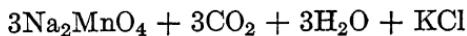
Manganese sulfide, MnS , is precipitated from an alkaline solution by H_2S or $(\text{NH}_4)_2\text{S}$. It is pink in color when first formed but changes rapidly by oxidation to the brownish hydrated form. The sulfide is soluble in dilute HCl.

Sodium peroxide readily oxidizes the manganous ion to the tetravalent state, forming $\text{MnO}(\text{OH})_2$, in quite the same way as atmospheric oxygen. The equation for the oxidation of $\text{Mn}(\text{OH})_2$ by Na_2O_2 may be formulated in the following way:



Certain other oxidizing agents will accomplish the same result; for example, bromine in alkaline solution is used in the analytical procedures for this purpose.

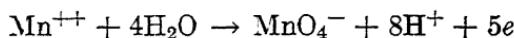
The oxidation of manganese to the hexavalent state is sometimes used as a test for this element. The oxidizing agent is KClO_3 , the reaction being carried out in a fused sodium carbonate bead. Sodium manganate, Na_2MnO_4 , green in color, is the oxidation product; the reaction is expressed by the equation:



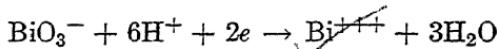
The corresponding ion, MnO_4^- , is the manganate ion, in which the manganese has an apparent valence of +6.

The oxidation of manganese to the permanganate form, that is, to MnO_4^- , is one of the most distinctive properties of this element as well as a most useful analytical reaction. The formation of the pink or purple ion is a very sensitive test for manganese and is, as well, the basis of several important quantitative methods for the determination of this element. Among the oxidizing agents used for this purpose are sodium metabisulfite, ammonium persulfate and lead dioxide.

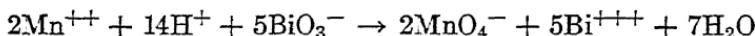
The oxidation of Mn^{++} to MnO_4^- by NaBiO_3 is expressed by the two electron equations,



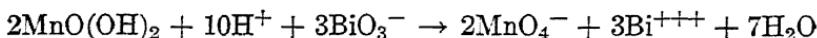
and



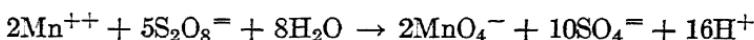
giving the balanced equation:



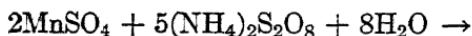
Likewise, for the oxidation of $\text{MnO}(\text{OH})_2$ by the same reagent we have



In the case of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ as the oxidizing agent, the equation for the reaction is



or, in molecular form,



This reaction proceeds only upon the addition of AgNO_3 which acts as a catalyst in the reaction.

The permanganate ion in the form of the reagent KMnO_4 is one of the most useful of analytical reagents, because it is one of the strongest oxidizing agents. The fundamental reaction, probably the most important property of manganese, is the reversible change expressed by the electron equation:



PRELIMINARY EXPERIMENTS

1. Action of Group Reagent on Manganous Solutions. To 2 drops of Mn(NO₃)₂ test solution add dilute NH₄OH. Note how the precipitate gradually changes color. Give the equations for the formation and oxidation of the precipitate.

Determine whether excess NH₄OH or added NH₄Cl have any effect on the solubility of the precipitate. Compare the action here with the effect of these reagents on nickel, cobalt and zinc test solutions.

2. Action of NaOH and Na₂O₂ on Manganous Salts. To a few drops of Mn(NO₃)₂ test solution add slowly a few drops of NaOH reagent. What is the substance formed? Try to dissolve it in an excess of the strong base. Is Mn(OH)₂ amphoteric?

Add a little sodium peroxide, dropping it from the tip of a spatula or knife blade into the test tube. To what is the brown color due? Give the equation for this oxidation.

3. The Bead Test for Manganese. Fuse some Na₂CO₃ in the loop of a platinum wire and dip it into the brown solid obtained in experiment 2. Heat the bead in a Bunsen flame until fusion takes place, and then touch the fused bead to some powdered KClO₃ and heat again. To what is the green color due? Write the equation.

4. The Bismuthate Test. To a drop of Mn(NO₃)₂ test solution add a drop of dilute HNO₃ and then drop into the tube a little powdered sodium bismuthate. Allow the suspended matter to settle, and note the color of the solution. Write the equation for the reaction.

5. The Persulfate Test. Place 1 or 2 drops of manganous test solution on the spot plate, add a drop of AgNO₃, acidify with dilute H₂SO₄, and then add a crystal of ammonium persulfate, (NH₄)₂S₂O₈. To what is the color due? Write the equation.

ALUMINUM, Al⁺⁺⁺

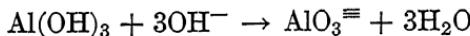
Aluminum, the third most abundant element and most abundant of all the metals, comprises about 8 per cent by weight of the earth's crust. It is present in all clays and soils and in many rocks and minerals, but the mineral used almost exclusively as the industrial source is bauxite, Al₂O₃·2H₂O. Workable deposits of this ore are found in various parts of the world, the primary economic deposits being in the United States, France, the Guianas, Hungary and Italy. It will be remembered that the free metal is obtained by dissolving purified bauxite in molten cryolite, Na₃AlF₆, and electrolyzing the resulting mixture.

The uses of metallic aluminum and its alloys are familiar to everyone. Aluminum oxide, in the form of emery, alundum and corundum, finds extensive use in abrasives and cutting wheels. Aluminum chloride serves as a catalyst in many industrial processes, including a method for the catalytic cracking of petroleum.

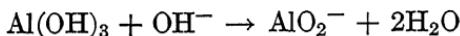
Aluminum sulfate and alum, $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$, are used to remove suspended material in water purification processes. Complex aluminum compounds constitute a large part of Portland cement.

Aluminum is always trivalent in its compounds and hence is not subject to oxidation or reduction to other ionic forms. The Al^{+++} ion, like other ions of invariable valence, is colorless. The common salts such as the chloride, nitrate and sulfate, are soluble in water.

When a hydroxide is added to a solution containing an aluminum salt, a colorless gelatinous precipitate is obtained. This precipitate usually is called aluminum hydroxide, and the formula $Al(OH)_3$ is applied to it, but in composition it is really a typical hydrated oxide of indefinite and undetermined composition. In its behavior it is a typical amphoteric hydroxide. In the presence of OH^- ions this substance acts as an acid and goes into solution, forming the orthoaluminate and meta-aluminate anion:

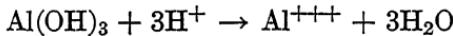


and

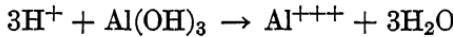
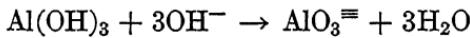


Since NH_4OH provides only a very low hydroxyl-ion concentration, its solvent action on $Al(OH)_3$ is scarcely noticeable; $NaOH$ and other alkalies that give a high hydroxyl-ion concentration dissolve it easily and completely. Moreover, since Al^{+++} forms no complex ion with NH_3 , $Al(OH)_3$ (unlike $Ni(OH)_2$, $Co(OH)_2$ and $Zn(OH)_2$) is hardly affected by NH_4OH .

In the presence of H^+ ion $Al(OH)_3$ acts as a base and goes into solution if the acidity is sufficient:

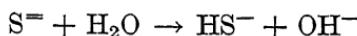


This is the other aspect of the amphoteric behavior of $Al(OH)_3$. The entire behavior can be summarized in the equations:



In this respect $Al(OH)_3$ resembles $Cr(OH)_3$ and differs from $Fe(OH)_3$ and $Mn(OH)_2$.

Addition of H_2S or a soluble sulfide to a solution containing Al^{+++} causes the precipitation of $\text{Al}(\text{OH})_3$ instead of the Al_2S_3 that might have been expected. This results from the basic nature of the sulfide ion:



Al^{+++} does not form an insoluble compound with HS^- , but it does with OH^- ; hence $\text{Al}(\text{OH})_3$ is precipitated.

A sensitive test for aluminum is the formation of an adsorption complex or "lake" with the dye "Aluminon," the trade name for the ammonium salt of aurin tricarboxylic acid. This dyestuff is strongly adsorbed by $\text{Al}(\text{OH})_3$, producing a bright red color. Alizarin and alizarin-S are two other dyes which produce lakes similar to aluminon with aluminum hydroxide.

Another test for aluminum is known as "Thenard's blue" test. This consists of igniting a roll of filter paper impregnated with $\text{Co}(\text{NO}_3)_2$ and $\text{Al}(\text{OH})_3$, whereby a blue-colored residue is produced. This product is probably a cobalt aluminate. Details for carrying out the test are given later.

Phosphates will precipitate AlPO_4 , which is soluble in bases as well as in strong acids, but insoluble in dilute acetic acid. Acetates will form $\text{Al}(\text{C}_2\text{H}_3\text{O}_2)_3$, easily hydrolyzed in dilute boiling solution to the basic acetate, $\text{Al}(\text{OH})_2(\text{C}_2\text{H}_3\text{O}_2)$. These properties must be kept in mind in the analysis of group III when phosphates are present.

Tartrates, citrates, sugars and many other organic substances of similar composition prevent the precipitation of $\text{Al}(\text{OH})_3$ by forming complex aluminum-organic ions. Such interfering substances must be removed in systematic analysis.

PRELIMINARY EXPERIMENTS

1. Action of Group Reagent on Aluminum Solutions. Add dilute NH_4OH to a few drops of the $\text{Al}(\text{NO}_3)_3$ test solution. What forms? Add an excess of NH_4OH . Is the precipitate noticeably soluble in this reagent?

To 3 drops of test solution add some NH_4Cl , and then dilute NH_4OH , slowly at first and then in excess. Does the precipitate redissolve? What is the function of the NH_4Cl ?

2. Amphoteric Nature of $\text{Al}(\text{OH})_3$. Add dilute NaOH dropwise to 5 drops of test solution. Note that $\text{Al}(\text{OH})_3$ is at first precipitated. Then add more NaOH . What happens? Give the equations.

Carefully neutralize the aluminate solution with dilute HCl . What forms? Add more HCl and record what happens.

3. Thenard's Blue Test. Take a strip of filter paper, dip it in $\text{Co}(\text{NO}_3)_2$ solution, touch it to precipitated Al(OH)_3 , roll it into the loop of a platinum wire, and burn it. Note the color of the ash.

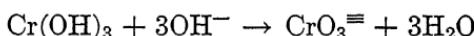
4. "Aluminon" Test. Precipitate some Al(OH)_3 by adding NaOH to the test solution. Dissolve the precipitate in the least possible amount of dilute HCl , and add 1 drop of ammonium acetate solution and then 1 drop of the Aluminon reagent. Mix thoroughly, and then make ammoniacal with dilute NH_4OH . Observe the change in color.

CHROMIUM, Cr^{+++}

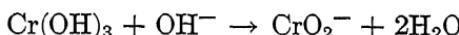
The element chromium occurs chiefly as the mineral chromite, $\text{Fe}(\text{CrO}_2)_2$, which is not widely distributed. Its chief use is in making chrome-alloy steels. Fusion of the ore with Na_2CO_3 in the presence of oxygen forms sodium chromate, Na_2CrO_4 , the starting point in the preparation of many chromium compounds.

The metal is very hard and very resistant to atmospheric corrosion, and for this reason is used in chrome plating. Stainless steel, armor plate and other alloys contain chromium, the chromium being introduced into the steel by adding ferrochrome, an alloy of iron containing 60 to 70 per cent of chromium.

From an analytical standpoint the most important forms of chromium are the chromic ion, Cr^{+++} ; the chromite, CrO_3^{\equiv} and CrO_2^- ; the chromate, CrO_4^- ; and the dichromate, Cr_2O_7^- , ions. Hydroxides produce from solutions containing chromic ions a gray-green precipitate of chromic hydroxide, Cr(OH)_3 , soluble in excess of alkali hydroxide, with the formation of either the ortho chromite ion,



or the metachromite ion,

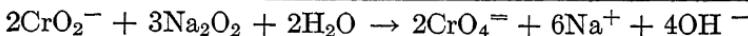
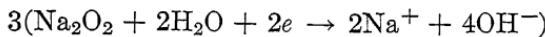
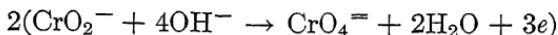


Since chromic hydroxide also dissolves in acids, it is a typical amphoteric hydroxide. Chromium does not form a complex ion with ammonia; hence Cr(OH)_3 is not soluble in excess of NH_4OH .

As in the case of aluminum, H_2S produces not the sulfide but the hydroxide. The explanation is the same as that given for aluminum.

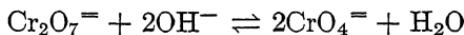
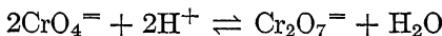
All tests for identifying chromium depend on the properties of the chromate, CrO_4^{\equiv} , and dichromate, Cr_2O_7^- , anions. The

change to these forms from the trivalent ions involves an oxidation; this usually is accomplished by the use of sodium peroxide, Na_2O_2 , in an alkaline solution:



Chromic acid, H_2CrO_4 ionizes in two stages forming the bichromate ion, HCrO_4^- and the chromate, $\text{CrO}_4^=$, ion.

The chromate and dichromate ions represent the same degree of oxidation of chromium. The change from one to the other is effected by changing the acidity of the solution. Chromates predominate in alkaline solution, and dichromates in acid solution. The reversible change of $\text{CrO}_4^=$ (yellow) \rightleftharpoons $\text{Cr}_2\text{O}_7^=$ (orange-red) can be shown by the equations:



Many chromates are insoluble. Among those of importance in analytical work are yellow PbCrO_4 , yellow BaCrO_4 and red Ag_2CrO_4 .

When H_2O_2 is added to a solution of a dichromate (or chromate) acidified with HNO_3 , an intense blue coloration appears. The color disappears in a few seconds, especially if the solution is warm, unless ether is present to remove it from the aqueous layer and stabilize it. The blue color lasts for a longer time in the ether layer but still disappears in a relatively short time. The blue compound is called perchromic acid. Its composition is not definitely known but probably is $\text{CrO}_3 \cdot \text{H}_2\text{O}_2$ or H_2CrO_5 .

PRELIMINARY EXPERIMENTS

1. Action of Group Reagent on Chromic Solutions. To 2 drops of chromic nitrate test solution add dilute NH_4OH . What is the pale green gelatinous precipitate? Write the reaction in ionic form. Try to dissolve the chromic hydroxide in an additional amount of NH_4OH . Does it dissolve?

To 2 drops of test solution add some NH_4Cl , and then dilute NH_4OH , slowly at first and then in excess. Does the precipitate appear to dissolve? In this respect it resembles what other hydroxides?

2. Amphoteric Nature of Cr(OH)₃. To 2 drops of Cr(NO₃)₃ solution add slowly a dilute solution of NaOH until a precipitate forms. What is it? Give the equation.

Continue the addition of the NaOH until the precipitate redissolves. Write the equation. The dissolving of Cr(OH)₃ in NaOH to form the orthochromite, CrO₃⁼, ion or the metachromite, CrO₂⁻, ion follows the behavior of Al(OH)₃ and Zn(OH)₂; this property is used to separate chromium and aluminum from iron and manganese.

Oxidation of Chromite ion to Chromate ion. Add to the sodium chromite solution a small quantity of Na₂O₂. Note the change of color from green to yellow. What has happened? Write the equation.

Acidify the chromate solution and note the change in color. What ion has formed?

3. Precipitation of BaCrO₄. Neutralize a portion of the chromate solution obtained in experiment 2, and then make it slightly acid with HC₂H₃O₂. Add a little NaC₂H₃O₂, and finally add BaCl₂. What forms? Supply the equation. This reaction enables one to separate chromium from aluminum.

4. The Hydrogen Peroxide Test for Chromate ion. To a drop of K₂CrO₄ solution acidified with dilute HNO₃, add several drops of ether and then, dropwise, several drops of hydrogen peroxide. Note the intense blue color in the ether layer; note also that it fades out quickly.

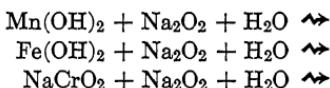
REVIEW EXERCISES GROUP IIIA

1. Give formulas of typical compounds of the elements of this subgroup, showing the various valence states of each element. Give the colors of the corresponding ions. In what periodic groups are they?

2. Are any of their hydroxides soluble in excess ammonia? Give the colors and formulas of the hydroxides. As hydrated oxides, what are their probable formulas?

3. By a series of equations show the effect of adding an equivalent amount of NaOH to Fe⁺⁺⁺, Mn⁺⁺, Al⁺⁺⁺⁺ and Cr⁺⁺⁺ ions. Which of these hydroxides dissolve in excess NaOH? Write the equations for those that dissolve.

4. Complete and balance the following equations using the ion-electron method:



What property is shown by the above reactions? Why do you not expect NaAlO₂ to react with Na₂O₂?

5. How would you separate: (1) iron from aluminum; (2) iron from nickel; (3) aluminum from zinc; (4) any cation of this group from the ions of group IV?

6. Write and balance electron equations to show: (1) the oxidation of ferrous ion; (2) the oxidation of chromic ion to CrO₄⁼ ion; (3) the oxidation of chromic ion to Cr₂O₇⁼ ion; (4) the oxidation of manganous ion to (a) MnO(OH)₂, (b) MnO₄⁼ ion, (c) MnO₄⁻ ion; (5) the oxidation of MnO(OH)₂ to MnO₄⁻ ion and to MnO₄⁻ ion.

7. Name some reagents which can be used to carry out the oxidations listed in exercise 6.

8. Make a list of two identifying or confirmatory tests for each of these four cations.

THE THEORY OF COMPLEX IONS

The Composition of Ions. Ions differ greatly in their chemical composition, as well as in the nature and number of their electric charges. The simplest ions consist of charged atoms; for example, the positively charged metal atoms such as Ag^+ , Cu^{++} , Ni^{++} , Fe^{++} and Fe^{+++} , and the negatively charged atoms of non-metallic elements such as the sulfide ion, S^- , and the halide ions, F^- , Cl^- , Br^- , I^- . On the other hand, two or more atoms of the same element may unite to form an ion, as, for example, the mercurous ion, Hg_2^{++} ; or atoms of different elements may unite into radicals, which, as charged ions, are of widely varying molecular complexity. Among these charged groups of atoms are many which in their chemical reactions behave as simple ions, as, for example, the ammonium cation, NH_4^+ , and such acid radicals as the cyanide, CN^- , the sulfate, SO_4^- , the arsenate, $\text{AsO}_4^{=}$, and the acetate, $\text{C}_2\text{H}_3\text{O}_2^-$, anions. There is yet another considerable group of ions of still greater complexity whose reactions and equilibrium relationships are extremely important in analytical procedures. To this latter group the term "complex ions" is applied.

Complex Ions. The most important complex ions encountered in qualitative analysis are those formed by the combination of metal ions with (a) ammonia (b) cyanide ions, (c) sulfide ions, (d) halide ions and (e) organic radicals. Examples of these complexes are cited in the following.

Complex Ions of Metals with Ammonia. Silver chloride dissolves in ammonia solution according to the reaction,



to form the complex diammono-silver ion.

Other similar complex ammines of considerable importance in qualitative analysis are those of copper $[\text{Cu}(\text{NH}_3)_4]^{++}$; of cadmium, $[\text{Cd}(\text{NH}_3)_4]^{++}$; of nickel, $[\text{Ni}(\text{NH}_3)_4]^{++}$; of cobalt, $[\text{Co}(\text{NH}_3)_4]^{++}$ and $[\text{Co}(\text{NH}_3)_6]^{+++}$; and of zinc, $[\text{Zn}(\text{NH}_3)_4]^{++}$.

Complex Metal-Cyanide Ions. A number of metallic ions form complex ions with the cyanide ion. The best known of these are the ferrocyanide ion, $[\text{Fe}(\text{CN})_6]^{=}$, and the ferricyanide ion,

$[\text{Fe}(\text{CN})_6]^\equiv$, which in the form of potassium salts are used as test reagents for iron, copper and other metals. Other complex cyanide ions are: the cuprous cyanide, $[\text{Cu}(\text{CN})_3]^\equiv$; the cadmium cyanide, $[\text{Cd}(\text{CN})_4]^\equiv$; the complex silver cyanides, $[\text{Ag}(\text{CN})_2]^-$ and $[\text{Ag}(\text{CN})_3]^\equiv$, and those of mercury, nickel, cobalt and gold, $[\text{Hg}(\text{CN})_4]^\equiv$, $[\text{Ni}(\text{CN})_4]^\equiv$, $[\text{Co}(\text{CN})_6]^\equiv$ and $[\text{Au}(\text{CN})_2]^-$.

Complex Metal-Sulfide Ions. When potassium hydroxide acts on certain sulfides such as As_2S_3 , the precipitate of arsenious sulfide dissolves and forms a mixture of the AsO_2^- and AsS_2^- ion, called the meta-arsenite and the metathioarsenite ions, respectively. Similar ions are formed from As_2S_5 , Sb_2S_3 , Sb_2S_5 and SnS_2 .

These complex metal-sulfide ions are analogous to the better-known oxy-anions of these elements. In fact, in composition they may be regarded as the oxy-ions (acid radicals) in which the oxygen has been replaced by sulfur. The analogy is shown in Table IX.

TABLE IX
Oxy-Ions *Thio-Ions*

Arsenite	AsO_3^\equiv	Thioarsenite	AsS_3^\equiv
Arsenate	AsO_4^\equiv	Thioarsenate	AsS_4^\equiv
Antimonite	SbO_3^\equiv	Thioantimonite	SbS_3^\equiv
Antimonate	SbO_4^\equiv	Thioantimonate	SbS_4^\equiv
Stannite	SnO_2^-	Thiostannate	SnS_3^-
Stannate	SnO_3^\equiv		

Other Complex Ions. Certain metal ions readily form complex ions with halide ions. Mercury, for example, forms the complex chloride, bromide and iodide ions, $[\text{HgCl}_4]^\equiv$, $[\text{HgBr}_4]^\equiv$, $[\text{HgI}_4]^\equiv$. In the precipitating agent used for potassium, H_2PtCl_6 , the platinum forms the complex chloroplatinate ion, $[\text{PtCl}_6]^\equiv$, with the chloride ion. Gold also forms complex halide ions. The chloro-ions of arsenic, antimony and tin are encountered in group II.

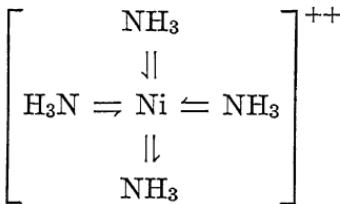
Complexes also form between certain metallic ions and organic radicals. The tartrate ion, in particular, has the tendency to combine with metals such as copper, antimony and aluminum, to form complexes, thereby interfering with tests for these metallic ions.

The Structure of Complex Ions. Covalence, and more particularly co-ordinate valence, are important in the discussion of complex ions, because it is by means of these two types of bonds that the parts of a complex ion are held together. To get some idea of the nature of this binding we may use for a simple example the

blue complex ion formed by adding a solution of NH_3 to a solution of a nickel salt, according to the reaction, using NiSO_4 :



The nickelous ion as it exists in the original solution has no electrons in the valence shell. The nitrogen atom in NH_3 has shared 3 of its 5 electrons with 3 hydrogen atoms, which gives it a total of 8 electrons in its valence shell and leaves a pair of electrons not shared with any atom. The NH_3 molecule, accordingly, shares this pair of electrons with the Ni^{++} ion; a similar action on the part of 3 other NH_3 molecules gives the ion a stable group of 8 electrons in its valence shell while still retaining its original charge. The condition in which the ion has a valence group of 8 electrons appears to be a more stable arrangement than that in which the valence group is entirely empty, so that the complex ion is a relatively stable ion. We may represent the complex ion as follows:



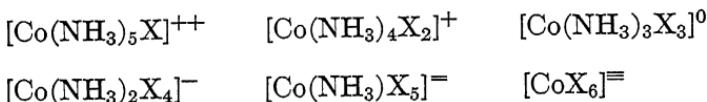
The NH_3 molecule when combined in a complex ion is called the ammono or ammine group, and so this complex ion is called the tetrammono-nickel ion or the nickel-tetrammine ion. As already indicated, the bonds holding the NH_3 molecules to the nickel ion are co-ordinate covalence bonds. A group of this kind is known as a co-ordinated group. The number of molecules or ions attached by co-ordinate valence to the central atom gives to the central element its co-ordination number; in the preceding example nickel has a co-ordination number of 4. Co-ordination numbers range from 2 to 8, with 4 and 6 by far the most frequent in occurrence. The co-ordinated group usually is distinguished from the rest of the molecule by being enclosed in brackets as in the formula $[\text{Ni}(\text{NH}_3)_4]\text{SO}_4$.

An important feature of the theory is that it is possible for a singly charged anion to take the place of one of the neutral molecules in the co-ordinated group, but, when this occurs, the charge on the co-ordinated group is changed by an amount equal to the charge on the replacing ion. Any ion so included in the co-ordin-

nated group loses many of its characteristic properties; chloride ion, for instance, is no longer precipitated when silver nitrate is added.

We may consider the application of these features to some specific compounds. For this purpose we may use for the central atom trivalent cobalt which has a maximum co-ordination number of 6 and forms a great number of complex ions. The complex ion formed with ammonia should have the formula $[\text{Co}(\text{NH}_3)_6]^{+++}$, but this happens to be only one of a series of complex ions containing cobalt and ammonia. This series is of no particular importance in itself, so far as we are concerned, but it illustrates so well the range of possibilities in the formation of such ions that we may be justified in examining it in some detail.

If we consider the $[\text{Co}(\text{NH}_3)_6]^{+++}$ ion and replace the ammonia molecules one by one by a singly charged anion, which we may designate by X , ions of the following compositions and charges will be obtained:



Many compounds containing these ions, X being Cl^- , NO_3^- , $\frac{1}{2}\text{SO}_4^-$ or some similar group, have been prepared. The changes in color of cobalt solutions when ammonium hydroxide is added may be interpreted as being due to a change from one to another of the foregoing ions.

The explanation of the formation of this series of compounds on the basis of the electronic theory is relatively simple. In the $[\text{Co}(\text{NH}_3)_6]^{+++}$ ion the cobalt ion has a co-ordination number of 6, that is, 6 pairs of electrons have been shared with it, 1 pair coming from each of the 6 NH_3 molecules. If, by some means, one of these NH_3 molecules were to be removed from the co-ordinated group and take with it both of the shared electrons, the cobalt ion would have an unsatisfied secondary valence, that is, an incomplete group of electrons, and would be in a position to form another co-ordinate bond with some other molecule or ion. The chloride ion, for example, having 4 pairs of electrons not shared with any atom, is able to supply the 2 electrons needed by the cobalt and accordingly enters the co-ordinated group. However, since the chloride ion carries one unit of negative charge, the net charge of the co-ordinated group is lowered by this amount, and the formula

$[\text{Co}(\text{NH}_3)_5\text{Cl}]^{++}$ results. Also, since the chloride ion now is attached by means of a co-ordinate bond, it no longer is able to give the reactions characteristic of the simple ion; for instance, it is not precipitated as AgCl when AgNO_3 is added. By a repetition of the previous process, until finally no more NH_3 molecules remain in the co-ordinated group, each of the other ions may be formed.

Throughout this discussion we have been speaking only of ions, but it probably has been noted that one member of the series is not an ion but a non-ionized compound. Compounds of this type, for example, $[\text{Co}(\text{NH}_3)_3(\text{NO}_3)_3]$, are those in which there have been introduced just enough negatively charged ions to compensate for the positive charge of the original ion, leaving the entire co-ordinated group uncharged or non-ionized and hence analogous to non-ionized organic compounds such as chloroform. Such non-ionized organic compounds are usually insoluble in water but soluble in ether or alcohol, distillable and rather inert chemically; similarly, compounds of the afore-mentioned type, even though they may be purely inorganic, are analogous in many points of behavior to the non-ionized organic compounds.

We have considered thus far only purely inorganic complex ions. There are, however, many organic molecules, such as urea, pyridine, ethylenediamine, hexamethylenetetramine and many others, which readily enter the co-ordinated group and give rise to the so-called metallo-organic compounds. Many of these organic compounds contain nitrogen, and it can be shown that usually, if not invariably, there is an unshared pair of electrons on the nitrogen atom, by means of which a co-ordinate bond may be formed with the central atom. The compounds that do not contain nitrogen also can be shown to possess such an unshared-electron pair at some point in the molecule. By making electronic diagrams,



the student may prove to himself that the groups $-\text{C}-$ and $=\text{N}-\text{O}-\text{H}$, for example, always contain such a pair on the oxygen and nitrogen atoms, respectively.

Such organic compounds as tartaric acid, citric acid and sugars interfere with the normal reactions of iron, cobalt and other metals. Examination of the formulas of these substances will show that



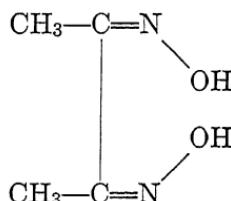
each contains several $-\text{C}-$ groups, which indicates that it is

possible for them to enter the co-ordinated group of the metal, form complex ions, and thus, as would be expected, give a behavior different from that usually attributed to the metallic ion itself. The formation of such complex ions, if they are distinctively colored, may serve as a qualitative test for the metal ion. Examples of this sort are found in the descriptions of the reactions of the metals.

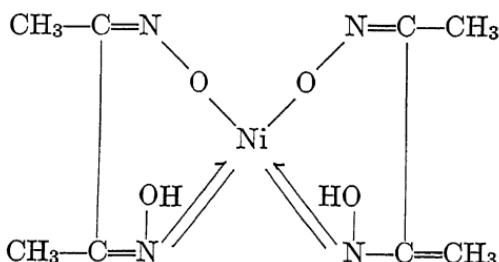
Chelate Compounds. Thus far in the discussion of complex ions and compounds we have mentioned only those in which a molecule in the co-ordinated group has but one point of attachment to the central atom. It is perfectly possible, however, for the same molecule to be attached to the central atom at two points, thus forming a ring structure. Compounds having such a structure have been called "inner-complex compounds" or "chelate compounds," the word chelate, meaning clawlike, suggesting the manner in which the molecule is attached to the central atom.

The molecule may be attached to the central atom by 2 covalent bonds, by 1 covalent and 1 co-ordinate bond or by 2 co-ordinate bonds. Of these three possibilities only the latter two will be considered here; we shall make no effort to distinguish between them, although it is possible to do so. The nature of these chelate compounds is best explained by consideration of a specific example.

Nickel, which commonly has a primary valence of +2 and a co-ordination number of 4, forms with dimethylglyoxime (see page 141).



a compound having the structure,



It will be noticed that each of the two organic molecules is attached to the nickel at two points forming 2 six-membered rings—a chelate compound. It is seen that nickel has taken the place of a hydrogen atom in each of the two organic molecules, forming covalent bonds with the oxygen atoms to which the hydrogen was originally attached. The originally unshared pair of electrons on the nitrogen atoms of the other two $=\text{N}-\text{OH}$ groups now forms 2 co-ordinate bonds with the nickel.

Dyeing with the use of a mordant and analytical tests depending upon such a process also may be explained as being due to the formation of chelate compounds. The Aluminon test for aluminum illustrates this. When Aluminon is added to an acid solution containing aluminum, the red color is distributed uniformly throughout the solution. The addition of ammonium hydroxide to this solution results in the formation of clumps of hydrated aluminum oxide which are colored bright red by the dye. The dye collects on the precipitate, leaving the solution practically colorless. Dyes which behave in this way have groups that favor the formation of chelate compounds, and, although frequently the actual structure of the colored material is totally unknown, it is highly probable that it is a chelate compound.

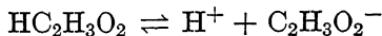
A material like hydrated aluminum oxide which combines with a dye and forms a stable-colored complex is called a mordant; the combination of a mordant and a dye is called a lake. Lakes frequently are described as being adsorption complexes, but it is probable that, in this case at least, "adsorption" is to be interpreted as an actual chemical combination.

By far the greater number of chelate compounds have rings containing 5 or 6 atoms. A ring of this size seems to give greater stability than one containing fewer than 5 or more than 6 atoms. Students of organic chemistry will recognize this fact as evidence in support of the Baeyer strain theory of ring formation.

Although the chelate compounds that are of the greatest importance in analytical chemistry are those that are insoluble in water, it must not be supposed that all of them are insoluble. On the contrary, such soluble materials as the complex compounds formed by iron and cobalt with tartrates and citrates are probably chelate compounds.

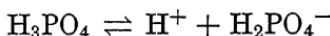
The Stability of Complex Ions. As already indicated (page 24) electrolytes dissociate (ionize) more or less into their respective

ions. Thus for a weak electrolyte, such as $\text{HC}_2\text{H}_3\text{O}_2$, which ionizes according to the reaction,



the extent of dissociation in a moderately dilute solution, is only about 1 per cent (1.34 per cent for a 0.1 *M* solution). The equilibrium relationships in such an ionizing system lead to important equilibrium constants known as ionization constants. Equilibria of this kind are discussed in Chapter V.

Ions which are composed of two or more elements or components, likewise, show a tendency to dissociate further into still simpler ions or components. For example, phosphoric acid yields, by its first stage of ionization,



H^+ ions and the dihydrogen-phosphate ion. This in itself feebly ionizes into H^+ ions and the monohydrogen-phosphate ion,



and this in turn ionizes though extremely feebly into H^+ and $\text{PO}_4^{=}$ ions. The ionizing tendency and the stability of ions such as H_2PO_4^- and $\text{HPO}_4^{=}$ also are treated as special cases of ionization equilibria in Chapter V.

Simple ions, that is, charged atoms, as already shown, can undergo change by being reduced or oxidized either to the atomic state or to some other valence state, through the gain or loss of electrons. Ions such as the $\text{SO}_4^{=}$, NO_3^- , $\text{C}_2\text{H}_3\text{O}_2^-$, $\text{PO}_4^{=}$, are extremely stable and show little or no tendency to dissociate or ionize into their components, though, if they contain an element of variable valence, they may be oxidized or reduced to other ionic forms.

Instability Constants. The equilibrium conditions which exist in solutions containing ions of the type designated as "complex ions," such as $[\text{Ni}(\text{NH}_3)_4]^{++}$, $[\text{Ag}(\text{NH}_3)_2]^+$, $[\text{Cd}(\text{CN})_4]^-$, $[\text{AsS}_2]^-$, $[\text{PtCl}_6]^-$, can be formulated as a direct application of the Law of Chemical Equilibrium, and are treated mathematically as special cases of ionization constants. The dissociation of a complex ion into its simpler components or ions reaches equilibrium when the ratio of the products of the concentrations of the component parts to the concentration of the undissociated complex ion reaches a definite value. This constant is called the instability constant; it

is, in fact, a special ionization constant. The instability constant is a measure of the tendency of the complex ion to dissociate into its components; if the value is very small, the tendency for ionization will be very slight.

In a solution in which a complex ion has formed, it is of considerable interest to know what concentrations of the simpler components exist in equilibrium with the complex ion itself. Thus for the reaction of the dissociation of the complex nickel-tetrammine ion,

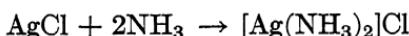


the equilibrium law takes the form,

$$\frac{C_{\text{Ni}^{++}} \times (C_{\text{NH}_3})^4}{C_{[\text{Ni}(\text{NH}_3)_4]^{++}}} = \text{Instability constant.}$$

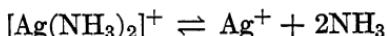
The value of this constant has been found by experiment to be 4.8×10^{-8} . Instability constants for a considerable number of complex ions of various types are given in Table XXIX. By suitable calculation we can determine the concentrations of the components which exist under specified conditions in equilibrium with each other. An important application of complex ions to analytical work is in the dissolving of various precipitates.

Example 1. Suppose we take 0.01 gram mole of AgCl and treat it with NH₄OH until it dissolves, according to the reaction:



What are the concentrations of Ag⁺ and NH₃ in equilibrium?

The concentration of the complex salt, [Ag(NH₃)₂] Cl is 0.01 M, and, if it is assumed that this complex salt is completely ionized, the concentration of [Ag(NH₃)₂]⁺ likewise will be 0.01 M. The complex ion ionizes to a slight extent according to the ionization reaction,



for which we can write the equilibrium expression,

$$\frac{C_{\text{Ag}^+} \times (C_{\text{NH}_3})^2}{C_{[\text{Ag}(\text{NH}_3)_2]^+}} = K_{\text{instab.}} = 6.8 \times 10^{-8}$$

If we let x equal the concentration of Ag⁺, then the NH₃ concentration is $2x$, and the concentration of Ag(NH₃)₂⁺ is $(0.01 - x)$.

However, since the ionization is known to be extremely small, we may express the concentration of $[\text{Ag}(\text{NH}_3)_2]^+$ simply as 0.01 M. We have then

$$\frac{x \times (2x)^2}{0.01} = 6.8 \times 10^{-8}$$

$$4x^3 = 6.8 \times 10^{-10}$$

from which $x = 5.5 \times 10^{-4}$. The concentration of Ag^+ is 5.5×10^{-4} and that for NH_3 is 1.1×10^{-3} gram ion per liter.

Example 2. What is the silver-ion concentration in a solution containing 0.01 gram mole of $[\text{Ag}(\text{NH}_3)_2]^+$ when the total NH_3 concentration is made 0.1 M?

The equilibrium is

$$\frac{C_{\text{Ag}^+} \times (C_{\text{NH}_3})^2}{C_{[\text{Ag}(\text{NH}_3)_2]^+}} = K_{\text{instab.}}$$

Letting x equal the C_{Ag^+} , we have

$$\frac{x \times (0.1)^2}{0.01} = 6.8 \times 10^{-8}$$

from which C_{Ag^+} is equal to 6.8×10^{-8} . Comparing the C_{Ag^+} in this case with that of example 1, where no excess of the NH_3 was present, we find that the value has decreased from 5.5×10^{-4} to 6.8×10^{-8} , a ten-thousand-fold decrease.

Example 3. What is the Ni^{++} ion concentration in a solution containing 0.1 gram mole of the complex $[\text{Ni}(\text{NH}_3)_4]^{++}$ ion and which is 0.1 M with respect to the total NH_3 concentration?

If we substitute in the equilibrium equation,

$$\frac{C_{\text{Ni}^{++}} \times (C_{\text{NH}_3})^4}{C_{[\text{Ni}(\text{NH}_3)_4]^{++}}} = 4.8 \times 10^{-8}$$

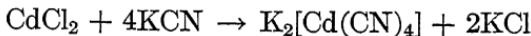
the known factors, $C_{[\text{Ni}(\text{NH}_3)_4]^{++}} = 0.1$ and $C_{\text{NH}_3} = 0.1$ we get for $C_{\text{Ni}^{++}} = x$,

$$\frac{C_{\text{Ni}^{++}} \times (C_{0.1})^4}{0.1} = 4.8 \times 10^{-8}$$

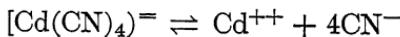
$$\frac{x \times 1 \times 10^{-4}}{1 \times 10^{-1}} = 4.8 \times 10^{-8}$$

$$x = 4.8 \times 10^{-3}$$

Example 4. What are the Cd⁺⁺ ion and CN⁻ ion concentrations in a solution obtained by treating a 0.1 M solution of a cadmium salt with KCN according to the reaction expressed by the following equation?



Since the cadmium salt solution is 0.1 M, the concentration of the [Cd(CN)₄]⁼ complex ion is also 0.1 M. The relation between the complex ion and its component ions,



is expressed by the equilibrium ratio,

$$\frac{C_{\text{Cd}^{++}} \times (C_{\text{CN}^-})^4}{C_{[\text{Cd}(\text{CN})_4]^=}} = K_{\text{instab.}} = 1.4 \times 10^{-17}$$

Letting $x = C_{\text{Cd}^{++}}$ and $4x = C_{\text{CN}^-}$, and substituting in the equilibrium we have

$$\frac{x \times (4x)^4}{0.1} = 1.4 \times 10^{-17}$$

By solving this equation, x is found to be 8.9×10^{-5} . The Cd⁺⁺ ion concentration is therefore 8.9×10^{-5} , and the CN⁻ ion concentration 3.6×10^{-4} gram ion per liter.

Example 5. What are the Cu⁺ ion and CN⁻ ion concentrations in a 0.1 M solution of K₂[Cu(CN)₃]?

As in the cadmium-cyanide complex-ion equilibrium, we have

$$\frac{C_{\text{Cu}^+} \times (C_{\text{CN}^-})^3}{C_{\text{Cu}(\text{CN})_3^=}} = K_{\text{instab.}}$$

$$\frac{x \times (3x)^3}{0.1} = 5 \times 10^{-28}$$

$$x = 3.7 \times 10^{-8}$$

The cuprous-ion concentration is 3.7×10^{-8} , and the CN⁻ ion concentration is three times this value or 1.1×10^{-7} gram ion per liter.

QUESTIONS AND PROBLEMS—SET 5. COMPLEX IONS

- Define and illustrate electrovalence, covalence and co-ordinate covalence. Write the co-ordinated formulas for (a) Co(NH₃)₆⁺⁺⁺; (b) Cu(NH₄)₄⁺⁺; (c) Cu(CN)₃⁼; (d) Fe(CN)₆⁶⁻.

2. Explain the theory of co-ordination in terms of electrons. Account for the formation of series of complex ions by replacement of ions or groups within the co-ordinated group.

3. Write equations to show how the following compounds are dissolved by treatment with the specified reagent:

- (a) AgCl dissolved by KCN
- (b) Cd(OH)₂ dissolved by KCN
- (c) Ni(OH)₂ dissolved by NH₃
- (d) As₂S₅ dissolved by (NH₄)₂S forming (NH₄)₃AsS₄.

4. How much KCN is required to dissolve 0.1 gram mole of Cd(OH)₂?

5. What volume of NH₃ solution (specific gravity 0.95 containing 12.74 per cent of NH₃ by weight) is required to dissolve 1.4334 grams of AgCl?

Ans. 2.81 ml.

6. Calculate the Ag⁺ ion concentration in a solution which is 0.1 M with respect to the complex salt Ag(NH₃)₂Cl. Assume complete ionization of the complex salt. $K = 6.8 \times 10^{-8}$

7. What is the NH₃ concentration in a solution which is 0.1 M with respect to the complex salt Ag(NH₃)₂NO₃, which may be assumed to be 87 per cent ionized?

Ans. 2.3×10^{-3}

8. What are the Ag⁺ and NH₃ concentrations in a 0.05 M solution of Ag(NH₃)₂NO₃, the solute being 87 per cent ionized?

9. Calculate the CN⁻ ion concentration in a solution 0.05 M with respect to the complex ion Cd(CN)₄⁻. The equilibrium is

$$\frac{C_{\text{Cd}^{++}} \times (C_{\text{CN}^-})^4}{C_{\text{Cd}(\text{CN})_4^-}} = 1.4 \times 10^{-17}$$

Ans. 3.1×10^{-4}

10. Calculate the CN⁻ ion concentration in a solution which is 0.05 M with respect to the complex ion Cu(CN)₃⁻. The equilibrium is

$$\frac{C_{\text{Cu}^+} \times (C_{\text{CN}^-})^3}{C_{\text{Cu}(\text{CN})_3^-}} = 5 \times 10^{-28}$$

11. A certain solution is 0.01 M with respect to Zn(NH₃)₄⁺⁺. The solution contains a total concentration of 0.1 gram mole of NH₃ per liter. What is the Zn⁺⁺ ion concentration?

$$\frac{C_{\text{Zn}^{++}} \times (C_{\text{NH}_3})^4}{C_{\text{Zn}(\text{NH}_3)_4^{++}}} = 2.6 \times 10^{-10}$$

Ans. 2.6×10^{-8}

12. What is the CN⁻ ion concentration in a 0.1 M solution of KAg(CN)₂, the complex salt being 85 per cent ionized?

$$\frac{C_{\text{Ag}^+} \times (C_{\text{CN}^-})^2}{C_{\text{Ag}(\text{CN})_2^-}} = 1 \times 10^{-21}$$

13. Is the Cd⁺⁺ ion concentration in a 0.05 M solution of Cd(NH₃)₄Cl greater or less than in a 0.05 M solution of K₂Cd(CN)₄? *Ans.* Greater

14. Calculate the [HgCl₄]⁼ ion concentration in a 0.05 M solution of H₂HgCl₄. $K = 1 \times 10^{-16}$

15. To what concentration is the cuprous ion reduced when a solution which is 0.05 M with respect to $\text{Cu}(\text{CN})_3^-$ is treated with CN^- so as to make the total CN^- concentration 0.001? $K_{\text{instab.}}$ of $\text{Cu}(\text{CN})_3^- = 5 \times 10^{-28}$

$$\text{Ans. } 2.5 \times 10^{-20}$$

16. If a small excess of KCN is added to a 0.1 M solution of $\text{K}_2\text{Cu}(\text{CN})_3$, such as to make the CN^- concentration 0.01, to what new concentration is the cuprous-ion concentration repressed?

17. If to a liter of solution containing 0.1 gram mole of $\text{K}_2\text{Cu}(\text{CN})_3$ and 0.1 gram mole $\text{K}_2\text{Cd}(\text{CN})_4$ there is added sufficient CN^- to bring the total CN^- ion concentration to 0.01, what will be the concentration of Cu^+ ion and of Cd^{++} ion?

$$\text{Ans. } C_{\text{Cu}^+} = 5 \times 10^{-23}$$

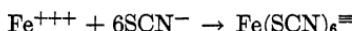
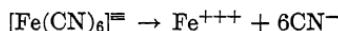
$$C_{\text{Cd}^{++}} = 1.4 \times 10^{-10}$$

18. In which solution will the silver-ion concentration be smaller, the one formed by dissolving 0.05 gram mole of AgCl with sufficient NH_3 to make the total NH_3 concentration equal to 0.01, or a solution formed by treating 0.05 gram mole of AgCl with KCN until the total CN^- concentration is 0.01?

19. Of the solutions containing, respectively, HgCl_4^- , HgBr_4^- and HgI_4^- complex ions, which solution has the smallest mercury-ion concentration? The instability constants are, respectively: 1×10^{-16} , 2.0×10^{-22} , and 5×10^{-31}

$$\text{Ans. } \text{HgI}_4^-$$

20. A solution of $\text{K}_3\text{Fe}(\text{CN})_6$ will not give the delicate thiocyanate test for ferric ion, but, if the solution is acidified with dilute HCl and then tested with KSCN, a test for ferric ions is obtained. Explain. The reactions involved are:



THE METALS OF THE AMMONIUM SULFIDE SUBGROUP: NICKEL (Ni^{++} , Ni^{+++}) COBALT (Co^{++} , Co^{+++}), ZINC (Zn^{++})

NICKEL, Ni^{++} (Ni^{+++})

The only commercial sources of nickel are found at Sudbury, Ontario, Canada, and on the island of New Caledonia in the South Pacific. The Sudbury ore is pentlandite, a complex mixture of the sulfides of nickel, iron and copper; the New Caledonia ore is a complex silicate.

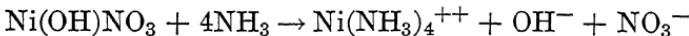
Nickel is used as a plating on iron and other metals and as a constituent of many alloys. Nickel-alloy steels are extensively used. Nickel is the catalyst used in the hydrogenation of oils to produce solid fats; it is also a constituent of the Edison storage cell.

The common valence of nickel is +2, in the nickelous ion, Ni^{++} . Trivalent nickel compounds are rare.

Ammonia solution when added in equivalent amount to a $\text{Ni}(\text{NO}_3)_2$ solution produces a greenish precipitate of the basic salt,



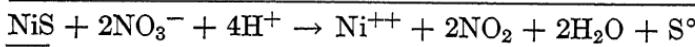
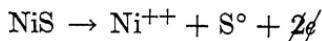
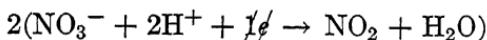
An excess of the reagent will dissolve the precipitate forming the complex ion whose structure already has been discussed:



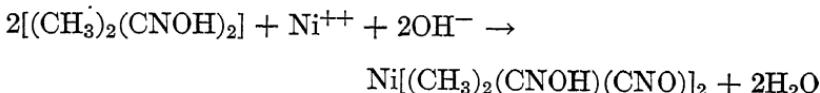
The complex tetrammono-nickel ion will form directly if the ammonia reagent contains a considerable quantity of ammonium salt, such as NH_4Cl or NH_4NO_3 .

In neutral or alkaline but not in an acidic solution, H_2S produces a black precipitate of nickelous sulfide. Nickel sulfide is peculiar in that it is not precipitated by H_2S from dilute HCl solution, and yet, after being precipitated from alkaline solution, it does not redissolve in dilute HCl, and dissolves but slowly and with difficulty in the concentrated acid. This is explained by the existence of three forms of the sulfide, α -, β - and γ - NiS ; the form first produced by H_2S is soluble in very dilute acids. Since no precipitate is obtained until the solubility-product constant of α - NiS is exceeded, nickel does not precipitate in a systematic analysis in group II. However, after being precipitated, it rapidly polymerizes, forming β - NiS which is soluble in 2 M HCl. This polymerizes still more, giving finally γ - NiS which is insoluble in acids unless oxidizing agents are present. An alternative explanation is that the substance first precipitated is $\text{Ni}(\text{HS})_2$; this would change into the less soluble NiS on standing. NiS dissolves slightly in NH_4OH , forming a brown solution; however, some of the color may be due to colloidal NiS , which forms quite readily unless ammonium salts are present.

NiS is so slowly attacked by dilute HCl that it is not dissolved to any appreciable extent by this solvent. It is, however, soluble in boiling concentrated HNO_3 , in aqua regia, or a mixture of KClO_3 and concentrated HCl, with which reagents it forms Ni^{++} and free sulfur. The reaction with HNO_3 is written as follows:



The best test for nickel is the reaction with dimethylglyoxime, which forms a flocculent red precipitate of nickel dimethylglyoxime. The test usually is conducted with an alcoholic 10 per cent solution of the reagent, in a solution faintly alkaline with ammonia. The reaction may be written in empirical form:

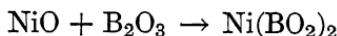


The structure of this chelate compound already has been discussed (page 132). This delicate test for nickel is the basis for the best method for the quantitative determination of nickel. Cobalt ions do not react in this manner; therefore this reaction is used as a test for nickel in the presence of cobalt.

A bead of fused borax, when touched to a bit of powdered nickel salt and held in the oxidizing part of the flame of a Bunsen burner, will be colored a reddish brown. Borax, when fused, undergoes decomposition, probably according to the reaction,



and forms a solid solution of boron trioxide in sodium metaborate. The nickel salt, such as $\text{Ni}(\text{NO}_3)_2$, likewise decomposes when heated to form NiO , which then reacts with the B_2O_3 to form nickel metaborate:



PRELIMINARY EXPERIMENTS

1. Action of Group Reagent on Nickel Solutions. To 2 drops of nickelous nitrate test solution add, drop by drop, a dilute solution of NH_4OH . Note that a greenish precipitate first forms. What is it? Give the equation for the reaction by which it is formed. Continue the slow addition of ammonia reagent until the precipitate dissolves, forming a solution which now contains the nickel in the form of tetrammonio-nickel ions. Write the reaction.

Effect of NH_4Cl . To 2 drops of test solution add a little NH_4Cl , and then slowly add NH_4OH . What happens? Explain the function of the NH_4Cl .

The effect of NH_4Cl on the solubility of the basic nickel compound also should be shown by precipitating a quantity of the basic salt and observing that it dissolves when sufficient NH_4Cl is present.

Precipitation of Nickelous Sulfide, NiS . Pass into the solution containing the deep blue complex ions a stream of H_2S . The first action of H_2S is to neutralize an equivalent amount of NH_4OH , producing $(\text{NH}_4)_2\text{S}$ which contains a high sulfide-ion concentration. The sulfide ion then reacts with the complex nickel ion, precipitating NiS . Show these steps by suitable equations.

Centrifuge off the NiS. The solution is sometimes brown, owing to the presence of colloidal nickel sulfide; the presence of NH_4Cl during the precipitation aids considerably in lessening the tendency toward the sol formation.

To a portion of the NiS add a crystal of KClO_3 and just enough concentrated HCl to dissolve the sulfide. Write the equation for the reaction.

2. Dimethylglyoxime Test. To a solution of $\text{Ni}(\text{NO}_3)_2$, made faintly ammoniacal with NH_4OH , add a few drops of dimethylglyoxime reagent. Describe the result. Ascertain the structure of the precipitate which forms.

3. Borax Bead Test. Make a small loop in the end of a platinum wire. Heat the loop to redness, touch it to a quantity of borax, and fuse it in the flame of a Bunsen burner. The operation may have to be repeated until a bead somewhat larger than a pinhead is obtained.

Allow the clear bead to cool, moisten it, and dip it into a very small quantity of powdered $\text{Ni}(\text{NO}_3)_2$. Then hold it in the oxidizing (outside) portion of the flame, and observe the result.

COBALT, Co^{++} ; Co^{+++}

In nature cobalt usually is found associated with iron and nickel. The principal ores are found in Ontario, Canada, and in the Belgian Congo.

Cobalt is familiar as the coloring material in blue "cobalt" glass. Its more important uses are as a constituent, along with chromium and tungsten, of Stellite, an alloy for making high-speed cutting tools. It is also present with tungsten carbide in carboloy, another cutting material. Cobalt steels are used for making very powerful magnets.

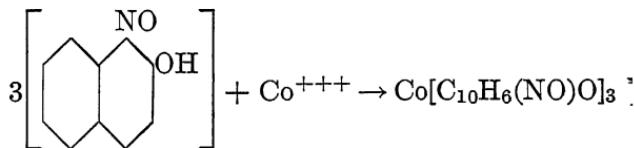
Cobalt forms both a di- and a trivalent series of salts, although the trivalent compounds, with the exception of double salts and complex compounds, are unstable and cannot be prepared in the solid form. The color of cobalt salts depends largely upon the degree of hydration, the hydrated salts being pink and the anhydrous blue.

Cobaltous hydroxide, $\text{Co}(\text{OH})_2$, is obtained as a blue precipitate when an alkali hydroxide such as NaOH is added to a solution of a cobaltous compound. The precipitate is not soluble in excess. Use of NH_4OH instead of a strong alkali illustrates an important property of cobalt, namely, its ability to form complex ions. A greenish precipitate of a basic salt, for example, $\text{Co}(\text{OH})\text{NO}_3$, is first formed, but readily dissolves in an excess, giving a reddish solution containing the $\text{Co}(\text{NH}_3)_6^{++}$ ion. This solution rapidly changes to a yellowish-brown color, owing apparently to the formation of the cobaltic hexammine ion, $\text{Co}(\text{NH}_3)_6^{+++}$, by oxidation. Upon boiling, the color changes to purplish red, caused by the

entrance of an anion into the co-ordinated group, forming an ion of the type $[\text{Co}(\text{NH}_3)_5\text{NO}_3]^{++}$. This complex-ion-forming property is illustrated further by the addition of concentrated HCl to a pink cobalt solution, whereupon the color changes to blue, owing apparently to the formation of the CoCl_4^- ion, although it also has been explained as a dehydration effect. HBr and HI give even more pronounced colors than HCl; these reactions have been used to detect cobalt.

H_2S forms in neutral or alkaline solution black CoS; no precipitate is obtained from acid solutions. CoS behaves toward acids in the same way as NiS, and for a similar reason.

A delicate test for cobalt is by use of the organic reagent, α -nitroso- β -naphthol. This reagent first oxidizes the cobalt ion to the trivalent cobaltic state. Then the hydrogen atoms from the hydroxyl groups from 3 molecules of the substance, as shown in the structural formula of the reagent, are replaced by a trivalent cobalt atom, forming cobaltic α -nitroso- β -naphthol:



The precipitate has a reddish-purple color. The reagent is a 50 per cent acetic acid solution of the compound. Nickel ion does not yield a precipitate with this reagent; hence the test for cobalt can be conducted in the presence of nickel.

Another test for cobalt is the reaction with KNO_2 . This reagent precipitates from acetic acid solutions a yellow compound, potassium cobaltnitrite, $\text{K}_3\text{Co}(\text{NO}_2)_6$. The student will recall that the formation of a similar compound is an important test for potassium. For making this test, the solution should be concentrated to a small volume, acidified with dilute acetic acid and saturated with KCl; then KNO_2 is added in excess. The acetic acid liberates HNO_2 , which decomposes with the formation of NO. The cobalt is oxidized to $\text{Co}(\text{NO}_2)_3$, which reacts with KNO_2 to form $\text{K}_3\text{Co}(\text{NO}_2)_6$. This test for cobalt can be made in the presence of nickel.

A borax bead will be colored a rich deep blue when cobalt is present. The probable composition accounting for the color is $\text{Co}(\text{BO}_2)_2$. See analogous property under nickel. This test will distinguish cobalt in the presence of moderate amounts of nickel.

A delicate test for cobalt is the thiocyanate reaction (the so-called Vogel's test), in which a blue color is formed, as a result of the formation of the $\text{Co}(\text{SCN})_4^-$ ion. This test works only in the absence of interfering ions. If ferric iron is present, a red color is obtained, but this interference may be overcome by reducing the iron to the ferrous state or by adding a fluoride, which removes it by forming the FeF_6^{3-} ion.

PRELIMINARY EXPERIMENTS

1. Action of Group Reagent on Cobalt Solutions. To 2 drops of cobaltous nitrate test solution add, in tiny amounts, dilute NH_4OH . The precipitate which forms first is not $\text{Co}(\text{OH})_2$, but a basic salt similar to that of nickel. Give the reaction. Record the color.

Continue to add ammonia until the precipitate dissolves. Note change in color. The brownish solution contains a complex ion whose composition is probably $\text{Co}(\text{NH}_3)_6^{4+}$. Heat the solution containing the complex salt. The change in color is due to the formation of a hexammono-cobaltic complex of the probable composition, $\text{Co}(\text{NH}_3)_6^{5+}$.

Effect of NH_4Cl . To 2 drops of test solution, add a quantity of NH_4Cl , and then slowly add NH_4OH . Describe the result.

Precipitate some of the basic salt with NH_4OH , and then add NH_4Cl . Note whether or not it dissolves.

Precipitation of Cobaltous Sulfide, CoS . Into the solution containing the brown complex pass H_2S . Write the equation. This result is the same as it would be from adding $(\text{NH}_4)_2\text{S}$ directly to a solution of cobalt containing an excess of NH_4OH .

Centrifuge and transfer the CoS already obtained to a crucible, and add KClO_3 and concentrated HCl . Does it dissolve? Write the equation for the reaction with this solvent.

2. Test With α -Nitroso- β -Naphthol. Acidify a few drops of cobalt test solution with dilute HCl , warm, and then add a few drops of the α -nitroso- β -naphthol reagent. Note the color of the precipitate and record its formula.

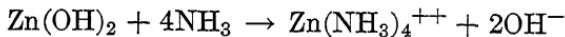
3. Borax Bead Test. Fuse some cobalt salt with borax held in the loop of a platinum wire. A blue bead of cobalt metaborate of the probable composition $\text{Co}(\text{BO}_2)_2$ should result. This test will distinguish cobalt in the presence of moderate amounts of nickel.

ZINC, Zn^{2+}

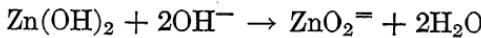
This useful metallic element occurs in nature chiefly as zinc blende, ZnS , and as the carbonate. A large portion of the world's supply is found in the United States. The metal is used extensively as a coating on sheet metal and wire and in many different alloys.

The element zinc is always divalent in its compounds; hence, as is to be expected, the zinc ion is colorless.

The hydroxide, $\text{Zn}(\text{OH})_2$, is precipitated when either NH_4OH or NaOH is added to a solution containing zinc ion. In an excess of ammonia, $\text{Zn}(\text{OH})_2$ dissolves to form a complex ion:

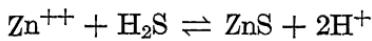


With an excess of NaOH or KOH the hydroxide dissolves to form the zincate ion:



Zinc hydroxide is likewise soluble in acids. Hence, like $\text{Al}(\text{OH})_3$ and $\text{Cr}(\text{OH})_3$, this hydroxide is typically amphoteric.

When H_2S is passed into a solution containing zinc ions, white ZnS is precipitated:



In the presence of a sufficient concentration of hydrogen ions ZnS will dissolve, since the reaction is markedly reversible. The addition of $\text{NaC}_2\text{H}_3\text{O}_2$ will decrease the solubility of the ZnS . Since $(\text{NH}_4)_2\text{S}$ can exist only in alkaline solution, this reagent produces essentially complete precipitation of ZnS .

The identification of zinc in the systematic scheme frequently gives trouble, not because of the lack of sensitive and satisfactory confirmatory reactions, but because of failure to secure a satisfactory separation from other ions of this group and from those of group II. Certain schemes of analysis base the final identification of zinc on the formation of the white sulfide; others rely on the ferricyanide test (Orange IV test) or the formation of Rinman's green.

Rinman's Green Test. This test depends upon the formation of a green ash when a piece of filter paper impregnated with a drop of zinc solution and very dilute cobalt acetate is burned. The green color is probably cobalt zincate, CoZnO_2 . As a modification, it has been recommended that a few long fibers of asbestos be dipped into the zinc solution, touched with a tiny drop of a very dilute cobalt nitrate solution, and then heated. Because of difficulty in securing the correct cobalt concentration when the test is carried out as described, the test may be performed on test paper impregnated with a cobalticyanide solution, which furnishes the correct cobalt concentration. If such test paper is available, place a drop of zinc solution on a square of it, and incinerate until all carbon is removed from the ash. Note the green color of the ash.

Ferricyanide Tests With Orange IV. Potassium ferricyanide, $K_3Fe(CN)_6$, when added to a zinc salt solution, forms a yellow or brown precipitate of zinc ferricyanide, $Zn_3[Fe(CN)_6]_2$. This reaction has been modified and made more sensitive by the use of organic reagents among which Orange IV is the best. The test with Orange IV is particularly sensitive if proper precautions are taken. The procedure is described in the following preliminary experiments.

PRELIMINARY EXPERIMENTS

1. Action of Group Reagent on Zinc Solution. Add dilute NH_4OH , dropwise, to a few drops of $Zn(NO_3)_2$ test solution until a precipitate forms. Write the equation for the reaction. Add an excess of NH_4OH . What happens? Give the equation.

Action of NH_4Cl . To 5 drops of the test solution add NH_4Cl and then NH_4OH . Does $Zn(OH)_2$ precipitate? Explain the result.

Precipitation of ZnS . Into this solution containing the complex zinc-ammonia ions pass H_2S . What is the white precipitate?

2. Amphoteric Nature of $Zn(OH)_2$. Dissolve the ZnS obtained in the previous experiment in dilute HCl, boil, and then add a few drops of NaOH. Note the precipitation of $Zn(OH)_2$. Continue adding NaOH until the precipitate dissolves. Like $Al(OH)_3$ and $Cr(OH)_3$, zinc hydroxide is amphoteric and, with an excess of strong base, forms zincate ions. Write the equation.

3. Rinman's Green Test. Cut a narrow strip from a piece of filter paper. Near one end place a drop of the zinc test solution, and then touch it with a tiny drop of cobalt nitrate solution. Roll up the strip, loop it into the platinum wire, and ignite in a flame. Examine the ash. A black ash indicates that too much cobalt reagent has been used.

4. The Orange IV Test. To a drop of the dyestuff, known as Orange IV, add one drop of dilute (1:24) H_2SO_4 (both reagents dispensed by the instructor) in a centrifuge tube and then 3 to 5 drops of a 2 per cent solution of potassium ferricyanide. The mixture now should have a red color. Then add to this mixture a drop or two of the zinc test solution. The color should change to greenish yellow in the presence of zinc.

REVIEW EXERCISES GROUP IIIB

- Give formulas for the simple ions and complex ammine ions of the elements of this subgroup, together with the colors of these ions.
- What are the valences of these 3 elements? Where are they found in the periodic table?
- In what respect does zinc differ from nickel and cobalt? Show this by their behavior with NaOH.
- Describe two identifying or confirmatory tests for nickel; for cobalt; for zinc.
- What single reagent can be used to separate each of the following pairs of ions: Ni^{++} and Zn^{++} ; Mn^{++} and Co^{++} ; Fe^{+++} and Co^{++} ; Ni^{++} and Al^{+++} ; Zn^{++} and Al^{+++} ?

OUTLINE OF METHOD OF ANALYSIS OF GROUP III 147

6. By a diagrammatic scheme show how the ions in the following mixture may be separated and identified: Fe^{+++} , Cr^{+++} , Zn^{++} , Ni^{++} , Al^{++++} .

7. A certain group III sample is colorless. What ions are absent? What ions may be present?

8. A certain group III unknown yields a precipitate which is completely soluble in excess NH_4OH and also in NaOH . What ion is present?

OUTLINE OF METHOD OF ANALYSIS OF GROUP III

The study of the properties of the ions of this group, followed by preliminary experiments, has revealed the basis upon which these cations are separated and identified. Moreover, the reactions of these elements and their compounds have given an experimental background for the important phenomena of oxidation and reduction, amphotерism and complex-ion formation, together with further applications of precipitation theory.

1. Upon the addition of an excess of NH_4OH [together with NH_4Cl which prevents the precipitation of $\text{Mg}(\text{OH})_2$ and decreases the solubility of $\text{Al}(\text{OH})_3$ and $\text{Cr}(\text{OH})_3$], the hydroxides of iron, manganese, aluminum and chromium are precipitated and remain so, whereas nickel, cobalt and zinc form complex ammoniums. This major separation is based on the tendency of these ions to form soluble complexes. The use of excess ammonia reagent, therefore, divides the ions of this group into two major subgroups.

2. By the combined use of NaOH and the strong oxidizing agent, Na_2O_2 , iron remains insoluble as $\text{Fe}(\text{OH})_3$, and manganese as hydroxylated oxide of manganese, $\text{MnO}(\text{OH})_2$, whereas $\text{Al}(\text{OH})_3$ dissolves to form the meta-aluminate ion, AlO_2^- , and the $\text{Cr}(\text{OH})_3$, first converted to the metachromite ion, is oxidized to the chromate, $\text{CrO}_4^=$ ion. The amphoteric nature of $\text{Al}(\text{OH})_3$ and $\text{Cr}(\text{OH})_3$ enables this subseparation to be accomplished.

Tests for iron and manganese, as prescribed in the procedure, are then applied to the precipitated $\text{Fe}(\text{OH})_3$ and $\text{MnO}(\text{OH})_2$, and, likewise, in the solution containing AlO_2^- and $\text{CrO}_4^=$, prescribed tests for aluminum and chromium are applied.

3. Nickel, cobalt and zinc in the form of the ammonium complexes then are precipitated with H_2S as NiS , CoS and ZnS , and thus separated from the ions of groups IV and V. These sulfides are dissolved in an oxidizing solvent, for which a mixture of KClO_3 and concentrated HCl is recommended.

4. Zinc is separated from nickel and cobalt by utilizing the amphoteric nature of $\text{Zn}(\text{OH})_2$.

These indicated separations of the group precipitate, together with the necessary subsequent treatment of the separated portions for the purpose of individual cation identifications, are combined and here summarized diagrammatically. The detailed procedure to be followed in the analysis of a mixture of ions of this group follows.

TABLE X

DIAGRAMMATIC OUTLINE OF ANALYSIS OF GROUP IIIA AND IIIB

Solution

Fe^{+++}	Fe(OH)_3	Fe(OH)_3	Dilute $\text{Fe}^{+++} + \text{K}_4\text{Fe}(\text{CN})_6 \rightarrow$ Prussian blue
Mn^{++}	$\underline{\text{Mn(OH)}_2}$	$\underline{\text{MnO(OH)}_2}$	$\text{HNO}_3 \quad \text{Mn}^{++} + \text{NaBiO}_3 \rightarrow \text{MnO}_4^-$ pink
Al^{+++}	NaOH	NaOH	
Cr^{+++}	Na_2O_2	Na_2O_2	<i>Solution</i>
			$\text{AlO}_4^- + \text{aluminon} \rightarrow$ red lake
	NH_4OH	Al(OH)_3	$\text{CrO}_4^- + \text{BaCl}_2 \rightarrow \text{BaCrO}_4$ yellow
		Cr(OH)_3	
NH_4Cl			
Ni^{++}	Centfg. $\text{Ni}(\text{NH}_3)_4^{++}$	NiS	$\text{Ni}^{++} + \text{dimethylglyoxime} \rightarrow$ red ppt.
		Conc. HCl	
Co^{++}	$\text{Co}(\text{NH}_3)_6^{+++}$	H_2S CoS	$\text{Co}^{++} + \alpha\text{-nitroso-}\beta\text{-naphthol}$ red ppt.
		Centfg. KClO_3	
Zn^{++}	$\text{Zn}(\text{NH}_3)_4^{++}$	NaOH ZnS	ZnO_2^{--} —Rinman's green
		Centfg. ZnS	

PROCEDURE FOR THE ANALYSIS OF GROUP III:
INTERFERING ANIONS ABSENT

Separation Into Subgroups and Precipitation of Division A. To 1 ml. of the sample add 5 drops of bromine water to oxidize to the ferric state any ferrous iron which may be present; boil to remove the excess of bromine. Then add a little solid NH_4Cl , make distinctly alkaline with concentrated ammonia solution, shake well, and finally centrifuge. Wash the residue twice with small portions of 1:1 ammonia, and add the washings to the centrifugate. The residue may contain any or all of the precipitated hydroxides: Fe(OH)_3 , MnO(OH)_2 , Cr(OH)_3 and Al(OH)_3 ; these are division A. The centrifugate may contain the ammines of nickel, cobalt and zinc: $\text{Ni}(\text{NH}_3)_4^{++}$, $\text{Co}(\text{NH}_3)_6^{+++}$ and $\text{Zn}(\text{NH}_3)_4^{++}$; reserve the centrifugate for later identification; this is division B.

ANALYSIS OF DIVISION A, GROUP III

Separation of Iron and Manganese from Chromium and Aluminum. Add 3 drops of water to the residue, add the same amount of NaOH solution, and then carefully add with spatula or penknife

a little Na_2O_2 . When effervescence ceases, centrifuge, and transfer the supernatant liquid to another centrifuge tube; the residue may contain $\text{Fe}(\text{OH})_3$ and $\text{MnO}(\text{OH})_2$; the solution may contain the meta-aluminate, AlO_2^- , ion, and the chromate, $\text{CrO}_4^{=}$, ion. Wash the residue with water until only a faint alkaline reaction is shown by litmus paper.

Dissolve the residue with 2 to 4 drops of dilute HNO_3 and 1 or 2 drops of 3 per cent H_2O_2 . Stir with a platinum wire. Add more H_2O_2 if complete solution is not obtained.

Detection of Iron. Place a drop of the afore-mentioned solution on a spot plate, and add 1 drop of dilute HCl and 1 drop of $\text{K}_4\text{Fe}(\text{CN})_6$. A precipitate of Prussian blue shows the presence of iron.

If the result of this test is doubtful, place another drop on drop-reaction paper or on the spot plate and add a drop of KSCN solution. A deep red color proves the presence of iron. A faint red color is due to iron as an impurity and should only be reported as a trace of iron.

Detection of Manganese. Add a drop of concentrated HNO_3 to another drop of the previous solution on a spot plate, and then an excess of solid sodium bismuthate. A purple coloration due to the formation of the MnO_4^- ion proves the presence of manganese.

If manganese is present in very small amounts in the original sample, it may escape precipitation with the iron and accordingly will be found with the cobalt and nickel. For this reason, provision is made in division *B* for testing for manganese if the results of the previous test should be negative or doubtful.

Detection of Chromium. Place a drop of the centrifugate obtained in the $\text{NaOH}-\text{Na}_2\text{O}_2$ treatment (the solution will be yellow if the chromate ion is present) on a spot plate, and add some solid $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ or BaCl_2 reagent. A yellow precipitate shows the presence of chromium.

Place 5 drops of ether in a test tube; then add a drop or two of the solution, a drop of concentrated HNO_3 , and finally several drops of hydrogen peroxide. A blue color in the ether layer is due to an unstable compound of chromium and peroxide and proves the presence of chromium.

Detection of Aluminum. Add dilute HNO_3 to a portion of the remainder of the centrifugate until it is just acid, and add solid $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$, 5 drops of aluminon reagent, and then NH_4OH .

until the solution is alkaline. Centrifuge. A red residue with partial removal of the red color of the solution shows the presence of aluminum.

ANALYSIS OF DIVISION B, GROUP III

Pass H_2S into the solution containing the nickel, cobalt and zinc (and possibly small amounts of manganese), until precipitation of sulfides is complete. Centrifuge, and remove the supernatant liquid to another centrifuge tube; boil the centrifugate to remove H_2S , stopper the tube, and set aside, if it is to be analyzed for groups IV and V. Wash the residue with warm water, and add the washings to the above liquid.

Dissolve the precipitated sulfides in concentrated HCl to which a small crystal of $KClO_3$ has been added.

Detection of Nickel. Place a drop of the solution on a spot plate, make ammoniacal with NH_4OH , and then add dimethylglyoxime reagent. A red precipitate of nickel dimethylglyoxime identifies nickel. The presence of nickel may be confirmed by the borax bead test. To carry this out, proceed as instructed under "Nickel—Preliminary Experiment 3," page 142.

Detection of Cobalt. On a spot plate make a drop of the solution ammoniacal, and then acid with $HC_2H_8O_2$. Add a drop of α -nitroso- β -naphthol solution. A reddish-brown precipitate shows the presence of cobalt. To another drop on the spot plate add 2 or 3 drops of alcohol, and then drop in a crystal of KSCN. A blue color proves the presence of cobalt.

[**Supplementary Test for Manganese.** In the absence of a positive test for manganese in division A, repeat the test described on page 149 for this cation with drop quantities of this solution.]

Detection of Zinc. To the remainder of the solution add one-half its volume of a 30 per cent solution of $NaOH$, and boil for several minutes. This will precipitate the cobalt, nickel (and manganese) as hydroxides, and leave the zinc in solution as the zincate ion. Centrifuge to remove the precipitated hydroxides, and test for zinc in the centrifugate.

Place a drop of the Orange IV reagent in a test tube, acidify it with a drop of dilute 1:24 H_2SO_4 , and add a few drops of a freshly prepared 2 per cent solution of potassium ferricyanide, $K_3Fe(CN)_6$. A red color should form in the mixture. Then add a drop of the solution to be tested for zinc. If the mixture now turns green, the presence of zinc is affirmed.

This test should be confirmed by Rinman's test. If cobalt cyanide test papers are not available, place a tiny drop of dilute cobalt acetate solution on a small strip of filter paper, add a drop of the solution to be tested, hold the impregnated paper in the loop of a platinum wire, burn, and observe the color of the ash. A green color confirms the presence of zinc.

CHAPTER V

IONIZATION EQUILIBRIA AND BUFFER ACTION: THE ELEMENTS OF GROUPS I AND II

This chapter is divided into three sections. The first section considers ionization, common-ion effect, calculations based on ionization constants, and the properties and detection of silver, mercury and lead. In the center part of the chapter are discussed buffered precipitation, precipitation calculations based on common-ion effect, and the properties of bismuth, copper, and cadmium. The last section of the chapter deals with the properties of tin, antimony and arsenic and the procedure of analysis of group II.

IONIZATION EQUILIBRIA

The student is already familiar with the general phenomena of ionization. As a special case of ionization, the dissociation of complex ions already has been considered in Chapter IV. We will now consider the ionization of weak electrolytes, the equilibrium relationships of which lead to definite equilibrium ratios known as ionization constants.

The Extent of Ionization. If the extent to which different acids, bases and salts ionize is compared for solutions containing equal gram-molecular weights of the solute and at the same temperature, it will be found that this varies considerably with different electrolytes. Electrolytes in moderately dilute solutions, in which the proportion of the ionized to the non-ionized part of the solute is large, are strong electrolytes. Examples of strong electrolytes are solutions of HCl, NaOH, NaCl and, as a general rule, most inorganic salts. On the other hand, weak electrolytes are those in which the tendency to ionize in moderately dilute solutions is relatively small, such as solutions of NH₃, HC₂H₃O₂, H₂S, H₂CO₃ and water itself.

Table XI shows the percentage of ionization of 0.1 *M* solutions of common acids, bases and salts. Note that for acids the degree or percentage of ionization varies from 92.0 per cent for HCl to 0.01

per cent for HCN, for solutions of the same concentration, and that the primary ionization for polyprotic acids takes place to a much greater extent than the secondary and tertiary. Note, too, that NaOH is typical of a strong "base," whereas NH₄OH is a weak

TABLE XI

PERCENTAGE IONIZATION OF COMMON ACIDS, BASES AND SALTS IN 0.1 M SOLUTION AT 18° C.

Acid	Ionization Reaction	Per Cent Ionized
Hydrochloric	HCl ⇌ H ⁺ + Cl ⁻	92.0
Nitric	HNO ₃ ⇌ H ⁺ + NO ₃ ⁻	92.0
Nitrous	HNO ₂ ⇌ H ⁺ + NO ₂ ⁻	8.0
Formic	HCHO ₂ ⇌ H ⁺ + CHO ₂ ⁻	4.5
Acetic	HC ₂ H ₃ O ₂ ⇌ H ⁺ + C ₂ H ₃ O ₂ ⁻	1.34
Hydrocyanic	HCN ⇌ H ⁺ + CN ⁻	0.01
Sulfuric	H ₂ SO ₄ ⇌ H ⁺ + HSO ₄ ⁻ HSO ₄ ⁻ ⇌ H ⁺ + SO ₄ ⁼	90.0 60.0
Oxalic	H ₂ C ₂ O ₄ ⇌ H ⁺ + HC ₂ O ₄ ⁻ HC ₂ O ₄ ⁻ ⇌ H ⁺ + C ₂ O ₄ ⁼	40.0 1.0
Carbonic	H ₂ CO ₃ ⇌ H ⁺ + HCO ₃ ⁻ HCO ₃ ⁻ ⇌ H ⁺ + CO ₃ ⁼	0.12 0.0017
Hydrosulfuric	H ₂ S ⇌ H ⁺ + HS ⁻ HS ⁻ ⇌ H ⁺ + S ⁼	0.05 0.0001
Phosphoric	H ₃ PO ₄ ⇌ H ⁺ + H ₂ PO ₄ ⁻ H ₂ PO ₄ ⁻ ⇌ H ⁺ + HPO ₄ ⁼ HPO ₄ ⁼ ⇌ H ⁺ + PO ₄ ²⁻	27.0 0.1 0.0001
Water	HOH ⇌ H ⁺ + OH ⁻	0.0000002
Base		
Sodium hydroxide	NaOH ⇌ Na ⁺ + OH ⁻	90.5
Ammonium hydroxide	NH ₄ OH ⇌ NH ₄ ⁺ + OH ⁻	1.31
Calcium hydroxide	Ca(OH) ₂ ⇌ Ca ⁺⁺ + 2OH ⁻	75.0
Salt	Examples	
Uni-univalent	KCl, NaNO ₃ , NH ₄ Cl, NaC ₂ H ₃ O ₂	80-85
Uni-bivalent	CaCl ₂ , K ₂ SO ₄ , etc.	65-75
Bi-bivalent	MgSO ₄ , CuSO ₄ , etc.	35-45

base. The behavior of salts depends upon the type, and, as a general rule, for such concentrations as usually are employed in laboratory reagents, the percentage of ionization is relatively large. A few salts, notably certain salts of mercury, lead acetate, ferric acetate and a few others, are exceptions in that their ionization is abnormally weak.

Ionization and Concentration. It already has been pointed out that the extent of ionization differs widely for different electrolytes in solutions of the same concentration. For the same electrolyte the ionization varies with the concentration if temperature and other factors remain unaltered. That is, the more dilute the solution, the greater will be the degree of ionization. If we take, for example, 1 liter of a 0.1 M solution of acetic acid, in which the extent of ionization is 1.34 per cent, and dilute it with 9 liters of water, the resulting solution will be only one tenth as concentrated, and, if we measure, by electric conductivity or other methods, the new degree of ionization, we will find it to be 4.17 per cent (at 18° C.). Further dilution will result in still greater ionization, until in extremely diluted solutions there is no further increase in ionization. When this point of infinite dilution is reached, the solution is 100 per cent ionized.

The variation of the degree of ionization with concentration is shown in Table XII for two strong acids, two weak acids, a strong base (NaOH), a weak base (NH_4OH) and a number of salts.

TABLE XII

VARIATION OF APPARENT PERCENTAGE IONIZATION WITH DILUTION
AT 18° C.

Electrolyte	Concentration of Electrolyte in Moles per Liter			
	1 M	0.1 M	0.01 M	0.001 M
HCl	80.0	92.0	97.2	99.0
HNO ₃	85.0	92.0	96.9	99.0
HCHO ₂ (at 25° C.)	1.5	4.5	13.4	35.8
HC ₂ H ₃ O ₂	0.4	1.34	4.17	11.7
NaOH	77.0	90.5	93.3	97.1
NH ₄ OH	0.4	1.31	4.07	11.7
NaCl	74.1	85.2	93.6	97.7
AgNO ₃	—	81.4	93.1	97.7
NaCHO ₂	59.5	85.4	93.1	—
NaC ₂ H ₃ O ₂	52.6	77.9	89.4	—
NH ₄ Cl	74.7	85.3	94.0	—
K ₂ SO ₄	—	67.3	88.2	93.7
MgCl ₂	—	72.8	85.1	93.9
MgSO ₄	—	40.3	59.6	82.3

Note that for the strong acids, for NaOH and for many of the salts, the ionization is nearly complete in 0.001 M solution, and that for the weak acids and NH₄OH much greater dilution than

shown here is required to bring about complete ionization. A solute is considered a strong electrolyte if the proportion of ions to the non-ionized fraction is large when the total amount of dissolved solute is relatively large. Acetic acid and ammonium hydroxide are not considered strong electrolytes, because it is only in extremely dilute solutions that the concentration of ions predominates over the concentration of non-ionized solute.

Ionization and Temperature. With an increase in temperature most electrolytes show a decrease in the percentage of ionization. Thus in 0.08 *M* solutions of HCl at 18° C. the percentage ionized is 93.2; at 100° C. it is 89.7. For the same conditions in the case of HC₂H₃O₂ the values are 1.5 per cent and 1.17 per cent, respectively. Water is an exception to this rule, the ionization increasing somewhat with rise in temperature.

Effect of Solvent on Ionization. Electrolytes ionize to a greater extent in water than in most other solvents. Water is also the commonest solvent. Other ionizing solvents are liquid ammonia, liquid hydrocyanic acid and liquid sulfur dioxide. The ability of a solvent to bring about ionization is related to its dielectric constant, and, in general, the greater the dielectric constant, the better the medium for the ionization of the solute to take place. The presence of other dissolved substances also influences the ionization of many solutes.

Ionization Equilibrium. Ionization can be regarded as a reversible chemical reaction between dissolved molecules and their respective ions, and, when equilibrium is reached, certain of the dissolved molecules are dissociated into ions at a reaction rate which is equal to the rate at which other ions combine to reform non-ionized molecules. We can indicate such an ionization reaction by means of the general equation,

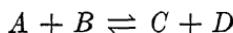


where *MA* stands for the dissolved non-ionized molecules of the compound *MA*, *M*⁺ for the cations and *A*⁻ for the anions in equilibrium with the non-ionized portion of the dissolved electrolyte. At equilibrium, which is quickly reached when the compound is dissolved, a certain fixed ratio between the non-ionized molecules and the products of their ionization always will be maintained.

The equilibrium equation,

$$\frac{C_C \times C_D}{C_A \times C_B} = K,$$

which expresses the equilibrium ratio of concentrations in the reaction,



may be transformed for the special reaction of ionization of an electrolyte MA :



into the special form:

$$\frac{C_{M^+} \times C_{A^-}}{C_{MA}} = K$$

K is an equilibrium ratio and expresses the ratio of the product of the ionic concentrations to the concentration of the non-ionized portion of the solute.

Equilibrium Ratios and Ionization Constants. One can write such an equilibrium ratio and determine its numerical value for any electrolyte, but the ratio will have the same constant value, for all ranges of concentration, for *slightly ionized electrolytes only*. For highly ionized acids and bases and for salts (which, with few exceptions, are highly ionized) the ratio is not constant. For slightly ionized acids, such as $\text{HC}_2\text{H}_3\text{O}_2$, HCN and HNO_2 , and for NH_4OH the ratio is practically constant for all concentrations. When the ratio is found to be constant (which is true only for a weak electrolyte), it is known as an ionization constant.

Thus, for a slightly ionized monoprotic acid, HA , which ionizes according to the equation,



the equilibrium condition is expressed by the ratio:

$$\frac{C_{\text{H}^+} \times C_{\text{A}^-}}{C_{\text{HA}}} = K_{\text{ion}}$$

In expanded form, the relation is

$$\frac{\text{Concentration of H}^+ \text{ ions} \times \text{concentration of anion}}{\text{Concentration of non-ionized molecules}} = K \text{ (ionization constant)}$$

As already stated, an electrolyte is characterized by a true ionization constant, only if the equilibrium ratios calculated for a number of concentrations have the same numerical value, that is, if

the ratios are practically the same for all concentrations. Whether or not an electrolyte conforms to the law of chemical equilibrium must be discovered by experiment and calculation.

Calculation of Ionization Constants. The calculation of the ionization constant of a weakly ionized acid is here illustrated, in examples 1 and 2, for acetic acid.

Example 1. Calculate the value for the equilibrium ratio of the components in a 0.1 *M* solution of $\text{HC}_2\text{H}_3\text{O}_2$.

This weak electrolyte ionizes according to the reaction,



or more simply expressed as a dissociation,



The extent of ionization at 18° C. is 1.34 per cent. (See Table XI, page 153). Since concentrations are computed from the molarity and percentage of ionization (see page 37), by means of the relationship,

$$M \times \alpha = \text{Concentration}$$

the respective concentrations in a 0.1 *M* solution of acetic acid are therefore: 0.1×0.0134 or 0.00134 gram ion of H^+ per liter; 0.1×0.0134 or 0.00134 gram ion of $\text{C}_2\text{H}_3\text{O}_2^-$ per liter; and 0.1×0.9866 or 0.09866 gram mole of non-ionized $\text{HC}_2\text{H}_3\text{O}_2$ per liter; this shows that, although the solution is 0.1 *M* in acetic acid, it is only 0.09866 *M* with respect to undissociated $\text{HC}_2\text{H}_3\text{O}_2$.

The equilibrium expression for acetic acid is

$$\frac{C_{\text{H}^+} \times C_{\text{C}_2\text{H}_3\text{O}_2^-}}{C_{\text{HC}_2\text{H}_3\text{O}_2}} = K$$

Placing the numerical values for the concentrations of the reacting substances in this expression gives the numerical ratio:

$$\frac{(0.1 \times 0.0134) \times (0.1 \times 0.0134)}{(0.1 \times 0.9866)} = 0.0000182$$

The value 0.0000182 or 1.82×10^{-5} is the equilibrium ratio for a 0.1 *M* solution of $\text{HC}_2\text{H}_3\text{O}_2$. If the equilibrium law holds for this electrolyte, substantially this same numerical value should be obtained for acetic acid solutions of other concentrations. Whether this is true will be discovered in the following example for a 0.01 *M* solution of $\text{HC}_2\text{H}_3\text{O}_2$.

Example 2. Suppose that we dilute a 0.1 *M* solution of acetic acid to ten times its volume, thus making a 0.01 *M* solution of acetic acid. What will be the equilibrium ratio?

One liter of this diluted solution will contain only one tenth as much dissolved solute as the first solution considered. If no change in the degree of ionization has taken place in this more dilute solution, a calculation of the ratio would give a new, different value for the equilibrium ratio and therefore not yield the same value as for a 0.1 *M* solution. But, the extent of ionization increases with dilution, and this means that the equilibrium, which became disturbed by dilution, again is restored by adjustment of the ratio between the concentrations of the ions and the non-ionized molecules. The extent of ionization of a 0.01 *M* solution of $\text{HC}_2\text{H}_3\text{O}_2$ at 18° C., from Table XII, page 154, is 4.17 per cent. The new concentrations are therefore 0.01×0.0417 or 0.000417 gram ion per liter of H^+ ; 0.01×0.417 or 0.000417 gram ion per liter of $\text{C}_2\text{H}_3\text{O}_2^-$; and 0.01×0.9583 or 0.009583 gram mole per liter of non-ionized $\text{HC}_2\text{H}_3\text{O}_2$. Inserting these values in the equilibrium expression gives

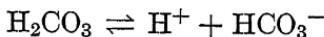
$$\frac{(0.01 \times 0.0417) \times (0.01 \times 0.0417)}{(0.01 \times 0.9583)} = 0.0000181$$

This new value for the ratio is in remarkably close agreement with the value calculated in example 1 for a 0.1 *M* solution and indicates that the equilibrium law holds rigorously for acetic acid solutions. The ratio has been determined for many other concentrations. The average value accepted over a wide range of molarities is 1.8×10^{-5} and is therefore the ionization constant for this weakly ionized acid.

Ionization constants for a number of weak electrolytes are given in Table XXXI in the Appendix.

Other acids that follow the equilibrium law more or less closely, namely, those that are only slightly ionized are H_2S , HNO_3 , HCN , H_2CO_3 , $\text{H}_2\text{C}_2\text{O}_4$, HAsO_2 , H_3AsO_4 , H_3PO_4 and H_3BO_3 . The more strongly ionized acids, such as HCl , HNO_2 , H_2SO_4 , do not yield the same ratio for different concentrations and thus deviate from the law; that is, they do not have true ionization constants. Diprotic weakly ionized acids such as H_2S , H_2CO_3 and $\text{H}_2\text{C}_2\text{O}_4$ which ionize in two stages have a primary and a secondary ionization constant.

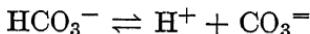
Thus, for carbonic acid, for its primary ionization,



the equilibrium expression is

$$\frac{C_{\text{H}^+} \times C_{\text{HCO}_3^-}}{C_{\text{H}_2\text{CO}_3}} = K' \quad (\text{primary ionization constant})$$

The bicarbonate ion further dissociates:

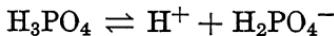


and for this secondary ionization the ratio is expressed by

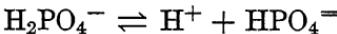
$$\frac{C_{\text{H}^+} \times C_{\text{CO}_3^{2-}}}{C_{\text{HCO}_3^-}} = K'' \quad (\text{secondary ionization constant})$$

The equilibrium relationships of H_2S , a slightly ionized diprotic acid, are extremely important. This reagent already has been used to precipitate NiS , CoS and ZnS and is the reagent for group II. It will be discussed more fully under the theory of the precipitation of sulfides with H_2S (see page 183).

Triprotic acids such as H_3PO_4 , H_3AsO_4 and H_3BO_3 have a primary, a secondary and a tertiary ionization constant, corresponding to the three stages of ionization. Thus, for H_3PO_4 , we have

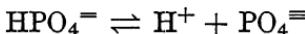


$$\frac{C_{\text{H}^+} \times C_{\text{H}_2\text{PO}_4^-}}{C_{\text{H}_3\text{PO}_4}} = K_1 \quad (\text{primary ionization constant})$$



$$\frac{C_{\text{H}^+} \times C_{\text{HPO}_4^{2-}}}{C_{\text{H}_2\text{PO}_4^-}} = K_2 \quad (\text{secondary ionization constant})$$

and



$$\frac{C_{\text{H}^+} \times C_{\text{PO}_4^{3-}}}{C_{\text{HPO}_4^{2-}}} = K_3 \quad (\text{tertiary ionization constant})$$

The primary stage of ionization takes place to a much greater extent than the secondary, and the secondary more than the tertiary; hence, the H^+ ion concentration of polyprotic acids is due largely to the primary ionization. Primary ionization constants of diprotic and triprotic acids are consequently numerically much larger than the secondary and tertiary constants. This will become evident from inspection of Table XXX.

The Ionization Constant of NH₄OH. The hydroxyl ion is the most important basic ion in qualitative analysis, and NH₄OH is the only commonly used hydroxide which can be considered as closely following the law. This reagent is used extensively; hence the equilibrium relationships are very important. The calculation of the ionization constant of NH₄OH is not so simple a matter as that for acetic acid, because in a solution of ammonium hydroxide there are, besides a low concentration of NH₄⁺ and OH⁻ ions, some non-ionized NH₄OH and dissolved NH₃. In the equilibrium formula for NH₄OH, the denominator actually is the sum of the concentrations of NH₃ and undissociated NH₄OH, but, if for simplicity both are expressed in terms of ammonium hydroxide concentration, the calculation of the constant is made the same as for acetic acid and leads to the simplified formula:

$$\frac{C_{\text{NH}_4^+} \times C_{\text{OH}^-}}{C_{\text{NH}_4\text{OH}}} = (K_{\text{ion}}) = 1.75 \times 10^{-5}$$

It is a coincidence that the ionization constant of NH₄OH is quite close to that for acetic acid. The discussion will be resumed later (see page 166).

Salts. Since salts, as a general rule, are strong electrolytes, no constant values of the equilibrium ratios are obtained for different concentrations. Of course, we can calculate a new value for each particular dilution, but, obviously, the theory cannot be applied in the same sense that we apply it, for example, to acetic acid, hydrogen sulfide and ammonium hydroxide.

The equilibrium of the ions of water, H⁺ ion and OH⁻ ion, is extremely important; this is considered in detail in Chapters VI and VII.

Calculations Based on Ionization Constants. If we represent the total molar concentration of the dissolved solute by *M* and the fraction of the solute that is ionized by α , the ionic equilibrium expression can be written in the form:

$$\frac{(M \times \alpha) \times (M \times \alpha)}{M \times (1 - \alpha)} = K_{\text{ion}}$$

$$\frac{M^2 \alpha^2}{M(1 - \alpha)} = K_{\text{ion}}$$

$$\frac{M \alpha^2}{1 - \alpha} = K_{\text{ion}}$$

In this form, the relationship between molar concentration and degree of ionization is known as the Ostwald dilution formula.

By means of this formula one can calculate (1) the ionization constant, (2) the molarity of the solution, (3) the percentage of ionization and (4) the ionic concentrations. Such applications are encountered frequently.

Example 3. Using the Ostwald dilution formula, calculate the ionization constant for $\text{HC}_2\text{H}_3\text{O}_2$ which in a 0.1 M solution ionizes 1.34 per cent.

Substituting 0.1 for M , and 0.0134 for α in $M \left(\frac{\alpha^2}{1 - \alpha} \right) = K_{\text{ion}}$, we have

$$0.1 \left[\frac{(0.0134)^2}{(1 - 0.0134)} \right] = K_{\text{ion}}$$

Solving this, we obtain

$$K_{\text{ion}} = 0.0000182 \text{ or } 1.82 \times 10^{-5}$$

If the ionization constant and one other factor are known, either the molarity or the degree of ionization can be calculated. Thus, from the Ostwald dilution formula, if K_{ion} and α are known, M , the molarity, can be found, or, conversely, if K_{ion} and M are given, α can be calculated.

Example 4. Calculate the molarity of a solution of $\text{HC}_2\text{H}_3\text{O}_2$, which is 1.34 per cent ionized, K_{ion} of $\text{HC}_2\text{H}_3\text{O}_2$ being 1.82×10^{-5} .

$$M \left[\frac{(0.0134)^2}{1 - 0.0134} \right] = 1.82 \times 10^{-5}$$

$$M = 0.1$$

The solution is therefore 0.1 M .

If we know the ionization constant and the molar concentration of the dissolved solute, we can calculate the degree of ionization by solving for α . Since α is very small for any weak electrolyte, $1 - \alpha$ will differ only slightly from 1, and hence very little error will be introduced by dropping α from the denominator. This avoids the solving of a quadratic equation. We have then approximately

$$M\alpha^2 = K_{\text{ion}}$$

$$\alpha = \sqrt{\frac{K_{\text{ion}}}{M}}$$

Example 5. What is the percentage of ionization of a 0.1 M solution of $\text{HC}_2\text{H}_3\text{O}_2$?

If we substitute in the foregoing equation:

$$\begin{aligned} 0.1\alpha^2 &= 1.82 \times 10^{-5} \\ \alpha^2 &= 1.82 \times 10^{-4} \\ \alpha &= \sqrt{1.82 \times 10^{-4}} \\ &= 0.0134 \end{aligned}$$

The solution therefore is 1.34 per cent ionized.

Calculation of the H^+ Ion Concentration in Solutions of Weak Acids. If the molarity and the ionization constant are known, the hydrogen-ion concentration readily can be found by first solving for α and then multiplying by the molarity.

Example 6. What is the H^+ ion concentration in a 0.1 M solution of $\text{HC}_2\text{H}_3\text{O}_2$, the K_{ion} being 1.82×10^{-5} ?

First find, by means of the Ostwald dilution formula, α , the degree of ionization as was done in example 5.

$$0.1 \left[\frac{\alpha^2}{1 - \alpha} \right] = 1.82 \times 10^{-5}$$

Since α is a small value, it may be dropped without serious error from the denominator and we have

$$0.1\alpha^2 = 1.82 \times 10^{-5}$$

or

$$\alpha = 0.0134$$

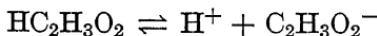
The solution is therefore ionized to the extent of 0.0134. Since the molarity is 0.1, the H^+ ion concentration is therefore

$$0.1 \times 0.0134 = 0.00134 \text{ gram ion per liter}$$

COMMON-ION EFFECT: BUFFER ACTION

In the ionization equilibrium formula it should be noted that the numerator of the ratio is the product of the gram-ion concentrations of the ions involved. In the particular cases calculated for $\text{HC}_2\text{H}_3\text{O}_2$ (examples 1 and 2) the concentration of the cation, H^+ , is equal to the concentration of the anion, $\text{C}_2\text{H}_3\text{O}_2^-$, merely because these values were obtained by measuring the ionization of

pure solutions of $\text{HC}_2\text{H}_3\text{O}_2$. That the concentrations of each set of ions need not necessarily be equal for equilibrium to be established has a very important application to actual analysis. The concentration of one set of ions may greatly exceed that of the other set of ions; important cases actually arise where it becomes desirable or necessary to add another compound containing ions of the same kind as the one or the other set already present. By this means the concentration of one ion can be adjusted to any desired value by varying the concentration of the other ion. The effect on the equilibrium of these added common ions is known as the *common-ion effect*. It is illustrated here in the case of $\text{HC}_2\text{H}_3\text{O}_2$. From the equation,



it is apparent that increasing the concentration of the acetate ion will, according to Le Chatelier's Law, displace the equilibrium toward the left, thereby increasing the concentration of the non-ionized $\text{HC}_2\text{H}_3\text{O}_2$ and decreasing the concentration of the hydrogen ion. The acetate-ion concentration may be increased by the addition of a highly ionized acetate, such as $\text{NaC}_2\text{H}_3\text{O}_2$ or $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$; hence, the addition of such a salt to a solution of acetic acid decreases the hydrogen-ion concentration and makes the solution less acid. A change of this type in the equilibrium of a weak electrolyte, caused by the addition of some substance which has an ion in common with the weak electrolyte, has the effect of repressing the ionization of the weak electrolytes and of maintaining a greatly decreased concentration of the opposing ion.

Evaluation of the Common-Ion Effect. In analytical procedures it is sometimes necessary to carry out a reaction in a solution of low hydrogen-ion concentration. A weak acid such as $\text{HC}_2\text{H}_3\text{O}_2$ yields, by virtue of feeble ionization, a low concentration of H^+ , but a still lower concentration can be secured by the addition of a highly ionized salt of acetic acid. That this must be the result can be seen from an actual calculation.

Example 7. What is the resulting H^+ ion concentration if to a liter of 0.1 M $\text{HC}_2\text{H}_3\text{O}_2$, which is ionized to the extent of 1.34 per cent, we add 0.1 mole of $\text{NaC}_2\text{H}_3\text{O}_2$, which in a liter of solution at 18° C. is about 80 per cent ionized?

We have at the outset 0.00134 gram ion of $\text{C}_2\text{H}_3\text{O}_2^-$ from the acetic acid and 0.080 gram ion of the same ion from the added sodium acetate, or a total of 0.08134 gram ion of $\text{C}_2\text{H}_3\text{O}_2^-$ ion.

There are also present initially 0.00134 gram ion of hydrogen and 0.09866 mole of non-ionized acetic acid. These substances cannot exist together in these proportions without disturbing the equilibrium, since the ionization constant must be satisfied. The only way in which equilibrium can be restored is for acetate ions to combine with hydrogen ions to form non-ionized acetic acid until the ratio again satisfies the equilibrium constant.

Let x equal the amount by which the H^+ and $\text{C}_2\text{H}_3\text{O}_2^-$ concentrations are decreased and the $\text{HC}_2\text{H}_3\text{O}_2$ concentration increased. Substituting in the equilibrium expression,

$$\frac{(0.00134 - x) \times (0.08134 - x)}{(0.09866 + x)} = 1.82 \times 10^{-5}$$

and solving this quadratic equation gives for x a value of 0.00129. The new hydrogen-ion concentration is therefore $0.00134 - 0.00129$ or 0.00005 gram ion per liter, showing a greatly decreased acidity.

By making certain approximations we can eliminate the necessity of solving this quadratic equation. Let y stand for the final hydrogen-ion concentration. Assume that the final acetate-ion concentration is that resulting from the added $\text{NaC}_2\text{H}_3\text{O}_2$ and that the final concentration of non-ionized $\text{HC}_2\text{H}_3\text{O}_2$ is the same as the molarity of the original acetic acid solution. These assumptions are warranted, since it can be seen from the foregoing that the deviation from the exact amounts (x in the calculation) is negligible. We have then

$$\frac{y \times (0.1 \times 0.80)}{0.1} = 1.82 \times 10^{-5}$$

and, solving this equation, we have

$$y = 0.0000227 \text{ gram ion per liter}$$

which is the new H^+ concentration by the approximate calculation.

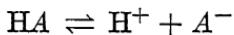
Just as an increase in the concentration of acetate ions will lower the concentration of hydrogen ions which can exist in equilibrium with acetic acid, an increase in the concentration of hydrogen ions, produced by the addition of a strong acid, will lower the acetate-ion concentration and repress the ionization of the acetic acid. Moreover, if a highly ionized acid such as HCl is added to a solution of an acetate, hydrogen ions together with acetate ions will be used up in forming non-ionized acetic acid. This is the way in which a highly ionized acid displaces a weaker acid from its salts; the

ionization of the less ionized acid is repressed by the hydrogen ions of the stronger acid.

The common-ion effect is applicable to all solutions of electrolytes in which the ionic concentrations are small because of either slight dissociation or slight solubility of the electrolyte.

Buffer Solutions. An important application of the common-ion effect is in controlling the acidity or basicity of a solution. A solution that contains both a weak acid and a salt which has the same anion as the weak acid will resist effects which tend to make it either more or less acid; and therefore the acidity of the solution remains approximately constant. The same is true of solutions containing a slightly dissociated hydroxide and a salt which furnishes the same cation as the hydroxide. Either type of combination is called a buffer mixture; a solution containing a buffer mixture is called a buffer solution.

The action of a buffer pair may be explained in the following way, by taking as an example a weak acid, HA , and one of its salts, MA . Consider the ionization equilibrium:



Any effect, such as the addition of a base, which tends to remove hydrogen ions will displace the equilibrium toward the right and result in the ionization of more HA and a (partial) restoration of the original hydrogen-ion concentration, accompanied by the neutralization of the added base. Similarly, if an acid is added to the mixture, the equilibrium is displaced toward the left, the excess hydrogen ions are removed by combination with some of the many anions provided by the salt, and the solution is left essentially unchanged in acidity. Thus, the non-ionized acid acts as a reservoir of hydrogen ions for neutralizing an added base, and the salt is a reservoir of the basic anion for neutralizing an added acid.

By using different acid-salt or hydroxide-salt combinations and proportions, it is possible to make a buffer solution which will have and maintain any desired value of acidity or basicity.

The Ammonium Buffer. In the same way that the addition of a salt of a weak acid to a solution of that acid will lower the hydrogen-ion concentration of the solution, so the addition of a salt of a weak base to a solution of a weak base will depress the hydroxyl concentration. Since NH_4OH is the only commonly used soluble weakly ionized base (a substance which furnishes a low concentration of the basic OH^- ion), the only practical case of common-ion

effect in a basic solution is the addition of an ammonium salt such as NH_4Cl or NH_4NO_3 to an ammonium hydroxide solution. Based on the equilibrium formula,

$$\frac{C_{\text{NH}_4^+} \times C_{\text{OH}^-}}{C_{\text{NH}_4\text{OH}}} = 1.75 \times 10^{-5}$$

the method of calculation is identical to that carried out for $\text{HC}_2\text{H}_3\text{O}_2$. Therefore one can calculate the OH^- ion concentration in a buffered ammoniacal solution if the concentrations of NH_4OH and added salt are known; or, conversely, if a certain predetermined concentration of OH^- ion is to be established and maintained, the amounts of ammonia solution and ammonium salt can be calculated. The following example illustrates the latter case.

Example 8. What quantities of ammonia solution and NH_4Cl should be used in order to prepare a liter of buffer solution so that the OH^- ion concentration will be maintained at 1.75×10^{-5} ?

First, let it be decided that a 0.1 *M* solution of NH_4OH will be satisfactory. This is prepared from the stock reagent of "concentrated" ammonia which has a specific gravity of 0.900 and contains 28.33 per cent of NH_3 (not NH_4OH) by weight. A 0.1 *M* solution of NH_3 , equivalent to a 0.1 *M* solution of NH_4OH , must contain 1.7 grams of NH_3 . From the relation:

$$\text{Vol. of } \text{NH}_3 \text{ solution} \times 0.900 \times 0.2833 = 1.7$$

there will be required 6.6 ml. of the concentrated reagent.

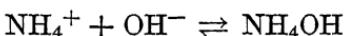
The amount of NH_4Cl now can be calculated. If we substitute in the NH_4OH equilibrium, in which 1.75×10^{-5} is the required OH^- ion concentration, and 0.1 the molarity of the NH_4OH , and the value, y , is the NH_4^+ ion concentration, the equation becomes

$$\frac{y \times 1.75 \times 10^{-5}}{0.1} = 1.75 \times 10^{-5}$$

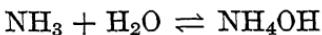
It can be seen by mere inspection that $C_{\text{NH}_4^+}$ is also 0.1 of a gram ion per liter. In this approximation method of calculation, the final concentration of NH_4^+ ion is assumed to be entirely derived from the added salt. On this basis, and if we assume further that the salt is completely ionized, there will be required 0.1 gram mole of NH_4Cl . The actual weight in grams will be 0.1×52.5 (the molecular weight of NH_4Cl) or 5.25 grams. If the actual extent of ionization of NH_4Cl is to be taken into account, we have 5.25 grams divided (not multiplied!) by 0.853, or 6.16 grams.

It is interesting and significant to point out, as illustrated in the preceding problem, that, when the OH^- ion concentration is equal to the ionization constant, the concentrations of non-ionized NH_4OH and added NH_4Cl are of the same magnitude.

An important application of buffering NH_4OH lies in the explanation of the equilibrium involved in the test for the NH_4^+ ion. It may be recalled that, to carry out this test, the ammonium salt solution is treated with a strong solution of NaOH , by which action NH_3 is evolved, and, when this comes into contact with a strip of moist litmus paper, it colors it blue. Adding a large concentration of OH^- ions from the highly ionized NaOH depresses the concentration of NH_4^+ ion, by common-ion effect; and results in the formation of NH_4OH .



But, as already mentioned, the NH_4OH equilibrium, in fact, depends upon the sum of the concentrations of NH_4OH and NH_3 , since the proportions in an aqueous solution depend upon the reaction of the water solvent:



Consequently, in order to maintain equilibrium in the equation,

$$\frac{C_{\text{NH}_4^+} \times C_{\text{OH}^-}}{C_{\text{NH}_4\text{OH}} + C_{\text{NH}_3}} = K$$

when C_{OH^-} is greatly increased, the value of C_{NH_3} is greatly lowered. This is accomplished by the evolution of gaseous NH_3 from the solution. If considerable ammonia is given off in the test, it is recognized by its odor. Otherwise, on reacting with the water in the moistened litmus paper, it forms NH_4OH which, by even its slight ionization, furnishes enough OH^- ions to affect the test paper.

QUESTIONS AND PROBLEMS—SET 6. IONIZATION CONSTANTS AND COMMON-ION EFFECT

1. Distinguish between equilibrium ratios and ionization constants. What differentiates a weak electrolyte from a strong electrolyte? Derive the Ostwald dilution formula.
2. What is buffer action? Explain how common-ion effect results in maintaining a constant concentration of a desired ion. If you wished to maintain a constant low hydroxyl concentration, what reagents would you employ?

3. By calculating the equilibrium ratios for the following solutions of HCHO_2 (formic acid), show that the value of K is substantially a constant:

<i>Molarity</i>	<i>Per Cent Ionized</i>	
(a) 1.0	1.5	<i>Ans.</i> 2.3×10^{-4}
(b) 0.10	4.5	2.1×10^{-4}
(c) 0.010	13.4	2.1×10^{-4}
(d) 0.0010	35.8	2.0×10^{-4}

4. Show that NH_4OH follows the equilibrium law and is characterized by an ionization constant by calculating the ratios of the following solutions of this weak electrolyte:

<i>Molarity</i>	<i>Per Cent Ionized</i>
(a) 1.000	0.400
(b) 0.100	1.31
(c) 0.0100	4.07
(d) 0.0010	11.7

5. Show by calculating the equilibrium ratios of the following solutions of NaOH that this strong electrolyte has no ionization constant:

<i>Molarity</i>	<i>Per Cent Ionized</i>	
(a) 1.000	77.0	<i>Ans.</i> 3.0
(b) 0.100	90.5	0.86
(c) 0.010	93.3	0.13
(d) 0.001	97.1	0.033

6. Show by calculating the equilibrium ratios of the following solutions of HCl that this strong electrolyte is not characterized by an ionization constant:

<i>Molarity</i>	<i>Per Cent Ionized</i>
(a) 1.000	80.0
(b) 0.100	92.0
(c) 0.010	97.2
(d) 0.001	99.0

7. Using the Ostwald dilution formula, calculate the molarity of a solution of NH_4OH which is 3.00 per cent ionized. $K_{\text{ion}} = 1.75 \times 10^{-5}$

$$\text{Ans. } 0.0189 \text{ M}$$

8. If a certain solution of formic acid, HCHO_2 , is 4.5 per cent ionized, what is its molarity? $K_{\text{ion}} = 2 \times 10^{-4}$

9. Applying the Ostwald dilution formula, calculate the degree (percentage) of ionization of a 0.05 M solution of NH_4OH . The ionization constant of this electrolyte is 1.75×10^{-5} .

$$\text{Ans. } 1.86 \text{ per cent}$$

10. Calculate the degree of ionization of a 0.15 M solution of HCN . The ionization constant is 7.2×10^{-10} .

11. Calculate the H^+ ion concentration in a 0.017 M solution of acetic acid. $K_{\text{ion}} = 1.82 \times 10^{-5}$

$$\text{Ans. } 5.6 \times 10^{-4}$$

12. What is the OH^- ion concentration in a 0.01 M solution of NH_4OH ? $K_{\text{ion}} = 1.75 \times 10^{-5}$. Use the Ostwald dilution formula, and check your answer with the ionization table.

13. If the H^+ ion concentration in a liter of 0.1 M $\text{HC}_2\text{H}_3\text{O}_2$ solution is not to exceed 2×10^{-5} , what must be the $\text{C}_2\text{H}_3\text{O}_2^-$ ion concentration? K_{ion} $= 1.82 \times 10^{-5}$ *Ans.* 9.1×10^{-2}

14. Suppose it is desired to maintain the OH^- ion in a solution of NH_4OH so that it does not exceed 1.0×10^{-5} gram ion per liter. If 0.10 M NH_4OH is used, how many grams of NH_4Cl must be added? Assume 87.0 per cent ionization of NH_4Cl .

15. What gram-mole quantity of $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ must be added to a liter of 1.0 M acetic acid solution in order to maintain the H^+ ion concentration at 1.0×10^{-5} if the salt is completely ionized? $K_{\text{ion}} = 1.82 \times 10^{-5}$

Ans. 1.8 gram mole

16. If there are 1.0 gram of $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ and 5.0 ml. of $\text{HC}_2\text{H}_3\text{O}_2$ (specific gravity 1.05, 99.15 per cent $\text{HC}_2\text{H}_3\text{O}_2$ by weight) present in 20.0 ml. of a solution, what is (a) the gram-ion quantity of $\text{C}_2\text{H}_3\text{O}_2^-$ ion present in the solution; (b) the $\text{C}_2\text{H}_3\text{O}_2^-$ ion concentration; (c) the H^+ ion concentration? Assume that the salt is 60 per cent ionized. Ionization constant of $\text{HC}_2\text{H}_3\text{O}_2$ is 1.82×10^{-5} .

17. Calculate the decrease in hydrogen-ion concentration when a 0.01 M solution of $\text{HC}_2\text{H}_3\text{O}_2$ is buffered by 0.1 gram mole of $\text{NaC}_2\text{H}_3\text{O}_2$. $\text{NaC}_2\text{H}_3\text{O}_2$ is 77.9 per cent ionized, and ionization constant for $\text{HC}_2\text{H}_3\text{O}_2$ is 1.82×10^{-5} .

Ans. 4.15×10^{-4}

18. If a certain solution is to maintain a hydroxyl-ion concentration of 1.5×10^{-4} , what reagents would you select and what quantities would you take for the preparation of a liter of this solution?

19. If a certain solution is to maintain a hydrogen-ion concentration of 1.0×10^{-5} what reagents would you select and what quantities would you take for the preparation of a liter of this buffered solution? *Ans.* Will vary

20. Magnesia mixture consists of 100 grams of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, 100 grams of NH_4Cl and 50.0 ml. of concentrated NH_4OH in 1 liter of solution. Calculate the OH^- ion concentration. Assume complete ionization of the two salts. $K_{\text{ion}} = 1.75 \times 10^{-5}$

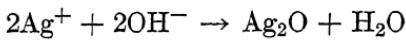
THE REACTIONS OF: SILVER (Ag^+), MERCURY (Hg_2^{++} , Hg^{++}), LEAD (Pb^{++})

SILVER, Ag^+

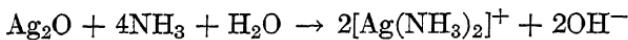
This precious metal is used in coinage and jewelry. In the form of compounds it finds application in photography and in medicine. The element is monovalent and produces the silver ion, Ag^+ . In the periodic table silver is found in the first group, along with gold and copper and the alkali metals. It is the only metal which exclusively belongs to cation group I in the analytical classification of the cations.

Most of the salts of silver are insoluble in water. The nitrate, the nitrite, the chlorate and the acetate are rather water-soluble. Silver nitrate is a widely used reagent, frequently employed in analytical procedures, as in the precipitation of halides.

The oxide, Ag_2O , is formed rather than the hydroxide, when a silver solution is treated with NaOH or KOH :

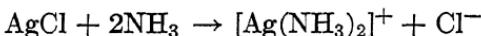


Ammonium hydroxide likewise produces the oxide, which is soluble in an excess of ammonia,



forming the complex diammono-silver ion. This ion has already been referred to in the section on instability constants (see page 133).

Silver chloride, AgCl , is precipitated as a curdy white solid when hydrochloric acid or any soluble chloride is added to a solution containing Ag^+ ion. Sunlight will cause silver chloride to darken. AgCl is insoluble in dilute acids but somewhat soluble in concentrated HCl . It is soluble in ammonia solution, forming the complex diammono-silver ion, $\text{Ag}(\text{NH}_3)_2^+$. The equation for the reaction is

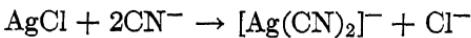


If a solution containing the complex chloride salt is neutralized with dilute HNO_3 , AgCl reprecipitates:

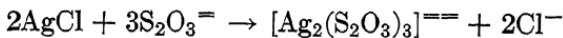


The dissolution of AgCl in ammonia solution enables one to separate AgCl from Hg_2Cl_2 , the method employed in the procedure of analysis. The reprecipitation of AgCl from such an ammoniacal solution constitutes the usual test for silver.

AgCl is also soluble in potassium cyanide and in sodium thiosulfate solutions. With KCN , the complex silver-cyanide ion forms



With $\text{Na}_2\text{S}_2\text{O}_3$, the "hypo" of the photographer, complex silver-thiosulfate ions are produced. The reaction is probably



AgCl is converted into Ag_2S by ammonium polysulfide, a property made use of in the anion scheme.

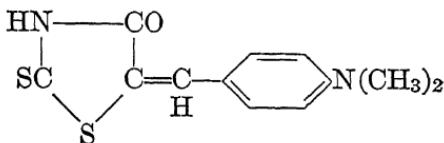
Silver bromide is somewhat more insoluble in water and in ammonia than AgCl . Silver iodide is still more insoluble in water than the other two halides and completely insoluble in ammonia. This relationship is utilized in the detection of the chloride, bromide and iodide ion in the anion scheme of analysis.

Hydrogen sulfide precipitates black silver sulfide, Ag_2S . Since H_2S is the precipitating agent for group II, it is important that silver be precipitated as completely as possible as AgCl in group I. Ag_2S is insoluble in HCl but dissolves in hot HNO_3 .

Ammonium carbonate, the reagent used in precipitating the alkaline earth elements, will precipitate Ag_2O .

Potassium chromate produces Ag_2CrO_4 , a rather insoluble red precipitate. This reaction has some applications in analytical chemistry.

A very delicate test for silver is the dimethylamino benzylidine rhodanine reaction. The organic reagent has the formula:



and produces a deep red or reddish-violet coloration with silver. The reagent also reacts with mercury, lead and copper salts, but it may be used as a specific test for silver by first adding a 5 per cent solution of KCN to the test solution and acidifying with dilute nitric acid. In a further modification of this test a suitably prepared collodion membrane is impregnated with the silver solution and the reagent, making the test extremely delicate.

PRELIMINARY EXPERIMENTS

1. Precipitation of Silver Chloride, AgCl . To a drop of the AgNO_3 test solution add dilute HCl , dropwise, until a precipitate no longer forms. Write the ionic equation for the reaction that takes place. Reserve the precipitate for further experiments. Determine whether NH_4Cl produces the same precipitate. Why is HCl used rather than NH_4Cl ?

Centrifuge the precipitated AgCl and discard the centrifugate. Add a few drops of water to the residue, and heat the mixture. Does the precipitate appear to dissolve to any appreciable extent in hot water? This property of AgCl is used to separate AgCl (and mercurous chloride as well) from PbCl_2 , the latter salt being soluble in hot water.

2. Reaction of AgCl With NH₄OH. Centrifuge, discard the water, and add to the AgCl a few drops of dilute ammonia solution. What happens? Explain the result. Write the reaction for the dissolving of AgCl in NH₃. This property of AgCl is used to separate silver chloride from mercurous chloride. The latter reacts in an entirely different way with this reagent.

3. Reprecipitation of AgCl as a Test for Silver. Gradually add dilute HNO₃ to the test tube containing the Ag(NH₃)₂Cl until the solution is acid. What happens when the solution is rendered acid? Give the equation.

4. "Rhodanine" Test. To a drop of silver nitrate test solution on a spot plate or on drop-reaction paper, add a drop of the reagent, dimethylamino-benzylidine rhodanine. Observe the color produced. To make this test more sensitive, repeat, first making the drop of test solution very slightly acid with dilute HNO₃.

MERCURY, Hg₂⁺⁺, AND Hg⁺⁺

This element occurs in nature chiefly in the form of sulfides. It is the only common metal which is liquid at ordinary temperatures and is the "quicksilver" of the alchemists. Mercury forms two series of compounds: namely, the mercurous, such as the oxide Hg₂O, the chloride and the nitrate, in which the element is monovalent, and the mercuric, in which mercury is divalent. In mercurous salts, the element is present in the form of the divalent group, ⁺Hg—Hg⁺, written Hg₂⁺⁺, rather than as the single monovalent charged atom, Hg⁺. In mercuric salts mercury is present as the divalent mercuric ion, Hg⁺⁺. The mercuric ion is a mild oxidizing agent, being reduced to the mercurous form:



Mercurous chloride, Hg₂Cl₂ (calomel), is insoluble in water and dilute HCl; on the other hand, mercuric chloride, HgCl₂ (corrosive sublimate), is soluble in water and dilute acids. For this reason, the mercurous ion belongs in analytical group I; the mercuric ion is a member of group II.

MERCUROUS ION, Hg₂⁺⁺

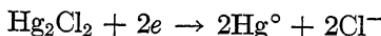
When a solution containing the mercurous ion, such as the test solution of Hg₂(NO₃)₂, is treated with a soluble chloride, such as HCl or NH₄Cl, very insoluble white Hg₂Cl₂ is formed:



This salt is insoluble, like AgCl, in hot water. It reacts with NH₄OH to produce a mixture of black metallic mercury and white

mercuric amido chloride, HgNH_2Cl . This is an internal *redox* reaction; one atom of mercurous mercury is reduced to the free metallic state, and the other is oxidized to the mercuric state.

The writing of the equation for this reaction is not so readily apparent and is demonstrated here. The reduction of the mercurous chloride to metallic mercury can be shown by the electron equation,

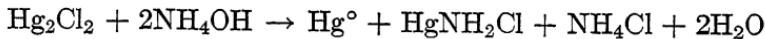


2 electrons being required to reduce Hg_2^{++} to 2Hg° . The oxidation of Hg_2Cl_2 to HgNH_2Cl is written as the other electron equation,



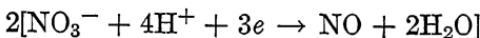
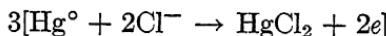
2 electrons being lost by Hg_2^{++} in becoming 2Hg^{++} .

Adding these 2 electron reactions and dividing the entire equation by 2 give

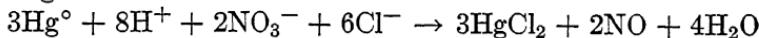


This mixture is soluble in strong oxidizing solvents such as aqua regia or a mixture of KClO_3 and concentrated HCl . In the case of its dissolution in aqua regia (a mixture of concentrated HNO_3 and concentrated HCl), both components are oxidized to the mercuric state. Here we have:

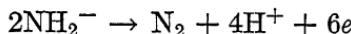
(1). *The oxidation of metallic Hg to HgCl_2 :*



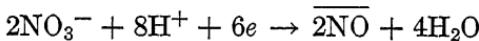
giving



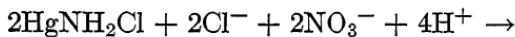
(2). *The dissolving of HgNH_2Cl .* The equation for the reaction can be balanced in the following manner: In the electron reaction,



the 6 electrons lost will reduce 2NO_3^- to 2NO :



The completed reaction is therefore



Although there are certain tests for the mercurous ion, these cannot be applied in the scheme of analysis, because, by the reactions indicated, the final identification is made for mercury as the mercuric ion.

MERCURIC ION, Hg^{++}

Mercuric salts, as a rule, are more soluble than the corresponding mercurous salts, although most of them are insoluble in water. The fact that mercuric chloride is soluble in water and dilute HCl places mercuric mercury in group II rather than in group I. Many of the mercuric salts are poisonous. Mercuric salts, as well as mercurous compounds, show a tendency to hydrolyze in aqueous solution; the test solution of $\text{Hg}(\text{NO}_3)_2$, for example, reacts with water to form the insoluble basic nitrate, $\text{Hg}(\text{OH})\text{NO}_3$. To prevent its formation, the test solution is kept strongly acid with HNO_3 . A solution of HgCl_2 is very slightly ionized; this is an exception to the general behavior of salts. In the presence of a large excess of chloride ion, HgCl_2 forms a complex ion represented by the formula, HgCl_4^- .

The most important compound of mercuric mercury, from an analytical standpoint, is the sulfide, HgS . When H_2S is passed into a solution containing the Hg^{++} ion, there is formed at first a white precipitate which gradually changes color and finally becomes black. These color changes are due to varying proportions of double salts of HgS and HgCl_2 , such as $\text{HgS}\cdot\text{HgCl}_2$. HgS is black and extremely insoluble in water and in HCl and HNO_3 , but somewhat soluble in alkalies like KOH. If HgS is boiled with dilute HNO_3 for some time, it will be transformed into a white insoluble double salt, $\text{Hg}(\text{NO}_3)_2\cdot 2\text{HgS}$.

Aqua regia or a mixture of KClO_3 and concentrated HCl is required to dissolve mercuric sulfide. The action of aqua regia can be understood best by consideration of the reaction involved. The products formed in the reaction are the slightly ionized HgCl_2 , free sulfur, NO and water. Like other reactions with aqua regia, this is a *redox* reaction. The balancing of the equation for the reaction is carried out as follows. As noted elsewhere, the constituent ions in aqua regia are NO_3^- , H^+ and Cl^- . For the electron equation involving the reduction of NO_3^- to NO we have



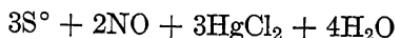
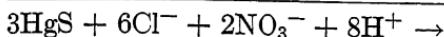
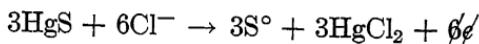
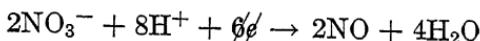
The oxidation of the sulfide ion in HgS to free S is represented by



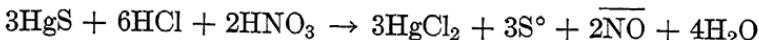
This equation when combined with the formation of HgCl_2 gives



To balance the electrons, equation (1) is multiplied by 2 and equation (3) by 3. Adding these and canceling out the electrons gives

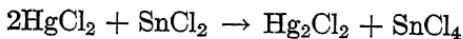


This ionic equation can be transformed readily into the following molecular one:

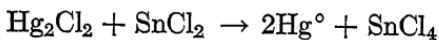


HgS is slightly soluble in KOH and forms the $\text{HgS}_2^{\text{--}}$ ion.

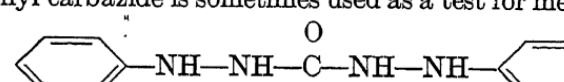
The usual test for mercury consists in the (successive) reduction of the mercuric ion by means of stannous chloride. When SnCl_2 is added slowly to a solution containing the mercuric ion, there first takes place a reduction to the mercurous state, accompanied by the precipitation of white Hg_2Cl_2 :



Further deduction to metallic mercury follows and causes the precipitate to become gray and finally black:



This test has been developed as a stain test by mixing a drop of the mercuric solution with a drop of aniline and adding this mixture to a drop of stannous chloride on drop-reaction paper; a black stain appears immediately.

Diphenyl carbazide is sometimes used as a test for mercury. The reagent,  yields a blue color with the mercuric ion.

A reagent of equal parts of KSCN and cobalt nitrate produces a distinctive blue precipitate, $\text{CoHg}(\text{SCN})_4$, with mercuric solutions.

PRELIMINARY EXPERIMENTS

1. Precipitation of Mercurous Chloride, Hg_2Cl_2 . Add dilute HCl to a few drops of $\text{Hg}_2(\text{NO}_3)_2$ test solution until precipitation is complete. Write the equation for the reaction.

Centrifuge, and to the residue add a little water, and heat the mixture. Does the precipitate dissolve in hot water? Compare the action of hot water here with that on AgCl , and bear this in mind when a corresponding experiment with PbCl_2 is performed. This behavior is used to separate Hg_2Cl_2 and AgCl from PbCl_2 .

2. Reaction of Hg_2Cl_2 with NH_4OH . Centrifuge the precipitate of Hg_2Cl_2 , and treat it with dilute ammonia solution. Does it dissolve? What change takes place? Show how the equation for the reaction is balanced. Compare the effect of NH_4OH on Hg_2Cl_2 with its effect on AgCl .

3. Dissolution of the "Black Residue." Remove the black mixture of Hg and HgNH_2Cl to a crucible. Prepare a small quantity of aqua regia by mixing 3 volumes of concentrated HCl with 1 volume of concentrated HNO_3 , and add several drops of this solvent to the residue. Heat the mixture until the solution is nearly evaporated to dryness. Show by separate equations how aqua regia dissolves mercury and mercuric amido chloride. The almost complete evaporation of the solution is necessary to decompose the excess of reagent and to remove the chlorine produced in the decomposition of the aqua regia. The presence of mercury can now be demonstrated in the almost completely evaporated solution by experiment 5.

4. Precipitation and Properties of Mercuric Sulfide, HgS . Neutralize 2 drops of mercuric nitrate, $\text{Hg}(\text{NO}_3)_2$, test solution, make slightly acid with HCl, and pass in H_2S . Account for the change in color of the precipitate. Write the equation for the formation of HgS .

Centrifuge, and wash the precipitate. Use separate portions of the precipitate for the following experiments.

Action of Potassium Hydroxide on HgS . To one portion of the precipitate, transferred to a test tube, add a drop of 4 M KOH reagent. This reagent is used in the systematic scheme used to separate the sulfides of group II into two subdivisions.

Does the HgS appear to dissolve in this reagent? Make a note of this property of HgS , and later compare the action of this solvent on the other sulfides of group II.

Action of Dilute HNO_3 on HgS . Treat another portion of the HgS with dilute HNO_3 . Heat the mixture gently at first. Does HgS dissolve? Continue boiling for some time. Account for any observed change in the precipitate.

Action of Aqua Regia on HgS . To a third portion of the precipitate add a drop of aqua regia, and heat if necessary in order to dissolve it. Write the reaction showing the method of balancing the equation.

5. Stannous Chloride Test for Mercury. Dilute the solution with a little water, and boil until chlorine is evolved or, alternatively, use a fresh portion

of mercuric test solution, and add, dropwise, stannous chloride reagent. Observe how the precipitate gradually changes color. What is first formed? To what is the darkening due? Supply the equations for the reactions taking place.

6. Diphenyl Carbazide Test. Place a drop of the carbazide reagent on the spot plate or on drop-reaction paper; add a drop of Na₂CO₃ reagent and then a drop of mercuric test solution. Record the result.

7. Double Thiocyanate Test. Place a drop of the reagent in a test tube, and add a drop or two of the mercuric test solution. What color is developed? What is the probable formula of the compound formed?

LEAD, Pb⁺⁺

Lead usually is found in nature in association with zinc. The chief mineral is galena, PbS. The metal finds many uses in alloys. Many of its compounds are technically of considerable importance. In its chemical properties, lead is much like tin, both belonging in the fourth group of the periodic table.

Lead forms two series of compounds, in which the element is respectively divalent and tetravalent. Thus, from the monoxide, litharge, PbO, are obtained the common salts such as Pb(NO₃)₂, PbCl₂ and PbSO₄. The hydroxide, Pb(OH)₂, is precipitated from Pb⁺⁺ solutions by NaOH; it is an amphoteric substance, reacting with acids to give Pb⁺⁺ ion and with bases to give the plumbite ion, PbO₂⁻. The dioxide, PbO₂, is typical of the tetravalent compounds of lead. The compound Pb(OH)₄ is plumbic acid, an amphoteric hydroxide. In the reactions utilized in the separation and detection of lead, only the divalent forms are involved.

Most of the salts of lead are insoluble in water, the notable exceptions being the nitrate, nitrite and acetate. Lead chloride is somewhat soluble in cold water and quite soluble in hot water. The bromide and iodide are less soluble in cold water than the chloride. Owing to the partial solubility of PbCl₂ in cold water, lead is not completely precipitated as lead chloride. In fact, if the amount of lead in a sample is not enough to give a precipitate of PbCl₂ with HCl, no separation as PbCl₂ in group I is at all possible, and small amounts of lead in samples are consequently detected only in group II. The sulfide, however, is very insoluble and enables one to precipitate lead almost completely as PbS.

Lead sulfide, PbS, is precipitated by H₂S from alkaline, neutral or slightly acid solutions as a black very insoluble substance. If the acidity is too great, either PbS will not precipitate, or else there will be formed a reddish-black double salt, PbCl₂·2PbS.

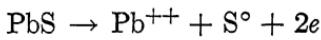
The sulfide is insoluble in cold dilute acids. Hot dilute HNO_3 will dissolve it with the formation of Pb ions, free sulfur and NO. In this respect it differs from HgS and shares this property with Bi_2S_3 , CuS and CdS . The solubility of PbS in HNO_3 is accounted for by the oxidizing action of the NO_3^- ion on the $\text{S}^=$ ion. The writing of the equation for this reaction is as follows: When PbS dissolves in warm dilute HNO_3 , the products of the reaction are Pb^{++} , free S, NO and H_2O . To balance the equation,



resolve it into two electron equations. For the oxidation of the sulfide ion, we have



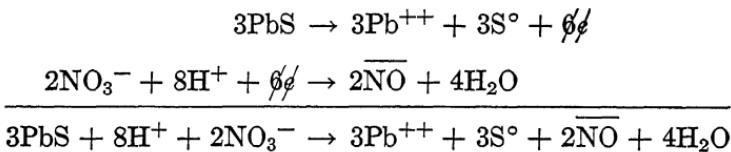
or combined with PbS ,



The reduction of the nitrate ion furnishes the second electron equation:



Multiplying, adding, and canceling electrons give the balanced equation in ionic form:



Expressed in molecular form, since 8H^+ require 8HNO_3 , the equation may be written

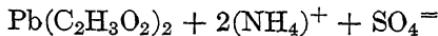
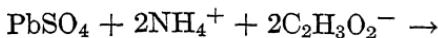


The important salts of lead from an analytical standpoint are PbCl_2 , PbCrO_4 , PbSO_4 and PbS .

Lead chromate is precipitated readily by K_2CrO_4 as a rather insoluble yellow salt. It is insoluble in acetic acid and in NH_4OH . This is the most characteristic test for lead.

Lead sulfate, PbSO_4 , is best precipitated by adding a large excess of H_2SO_4 . The precipitation of PbSO_4 enables one to separate lead from bismuth, copper and cadmium, the latter sulfates being soluble. Its formation can be applied as another test for lead. It is

soluble in ammonium acetate, owing to the formation of slightly ionized lead acetate:



PRELIMINARY EXPERIMENTS

1. Precipitation of Lead Chloride, PbCl₂. To 5 drops of Pb(NO₃)₂ test solution (5 mg. per ml.) add dilute HCl. Write the ionic equation for the reaction.

Centrifuge, add 2 drops of water, and heat to boiling. Note what happens. How does the action here differ from that for AgCl and Hg₂Cl₂? Allow the solution to cool. What are the needle-like crystals which form?

2. Precipitation and Properties of Lead Sulfide, PbS. Add a small drop of dilute HCl to some Pb (NO₃)₂ test solution, and pass in H₂S. Write the ionic equation for the formation of PbS. Repeat the experiment, doubling the quantity of HCl. Explain the result.

Action of Potassium Hydroxide on PbS. Centrifuge the PbS obtained in the first part of the preceding experiment, and divide into two portions. To one portion add some KOH. Is there any apparent action?

Action of Dilute HNO₃ on PbS. Add dilute HNO₃ to the other portion of the precipitate, and warm the mixture. How does the action differ from that of HgS? Write the equation, showing the steps involved in the balancing.

3. Properties of Lead Sulfate, PbSO₄. Add 5 drops of dilute H₂SO₄ to 2 drops of test solution in a crucible, and evaporate until dense white fumes of SO₃ are evolved. Cool, and pour the solution into cold water. What is the white precipitate? Write the reaction for its formation. This is the method of separating lead from bismuth, copper and cadmium, since the sulfates of the latter 3 ions are soluble in water and dilute H₂SO₄.

Centrifuge the PbSO₄ and treat with hot dilute ammonium acetate, NH₄C₂H₃O₂, solution. Explain why PbSO₄ dissolves in this reagent.

4. Potassium Chromate Test. To a few drops of Pb⁺⁺ test solution add a drop of K₂CrO₄ reagent. Write the equation.

REVIEW EXERCISES. GROUP I

1. To what groups of the periodic table do these three elements belong? What valences do they show? Give formulas for their ions. Which element forms anions?

2. Write equations showing the dissolving of Pb(OH)₂ and Pb(OH)₄ in NaOH. What property is shown here?

3. Write electron equations showing the oxidation and reduction of the ions (*a*) of mercury and (*b*) of lead.

4. What properties and preliminary experiments suggest a method of separating (*a*) silver from mercurous mercury; (*b*) lead from silver? Write the necessary equations.

5. Write balanced equations showing the dissolving of (a) metallic Hg, (b) HgNH_2Cl , and (c) HgS in aqua regia.
6. Give equations showing the separation and identification of silver.
7. Give equations for two precipitation tests for lead.
8. If a practice mixture contains 1 milligram of Ag^+ , 1 milligram of Hg_2^{++} and 5 milligrams of Pb^{++} , what weight in milligrams of HCl is required to produce complete precipitation of these ions? If the dilute hydrochloric acid has a specific gravity of 1.070 and contains 14.17 per cent of HCl by weight, what volume of acid is necessary to effect precipitation?
9. Calculate the chloride-ion concentration required to start the precipitation of Hg_2Cl_2 in a solution which contains 1 milligram of Hg_2^{++} per milliliter $K_{\text{s.p.}}$ of Hg_2Cl_2 is 2×10^{-18} .
10. What volume of dilute HCl solution (specific gravity 1.100) will be required to precipitate completely, as Hg_2Cl_2 , 50 milligrams of Hg_2^{++} ion?

OUTLINE OF THE METHOD OF ANALYSIS OF GROUP I

In a systematic analysis of cation solutions, the first step is the addition of dilute HCl, which will precipitate silver as AgCl , mercury, if present in the mercurous form as Hg_2Cl_2 ; if more than 1 milligram per milliliter of lead is present, some of it will be precipitated as PbCl_2 . This group is known as the hydrochloric acid group. (Mercuric ion as well as the unprecipitated lead will remain in solution, to be precipitated later by H_2S in group II.)

The separation of the chlorides from each other depends upon the following facts:

1. PbCl_2 is very soluble in hot water; AgCl and Hg_2Cl_2 are not. This property therefore serves to separate lead from silver and mercurous mercury. The presence of lead then can be shown by the precipitation of PbCrO_4 and PbSO_4 .

2. AgCl is soluble in NH_4OH forming the $\text{Ag}(\text{NH}_3)_2^+$ ion, whereas Hg_2Cl_2 undergoes a change to an insoluble mixture of HgNH_2Cl and Hg. Ammonium hydroxide therefore is used to separate AgCl from Hg_2Cl_2 . If the solution of the complex salt, $\text{Ag}(\text{NH}_3)_2\text{Cl}$, is neutralized by HNO_3 , AgCl is reprecipitated; this constitutes a test for silver.

3. The product formed by the action of NH_4OH on Hg_2Cl_2 is a black mixture, consisting of metallic mercury and mercuric amido chloride, HgNH_2Cl . Both constituents can be dissolved in aqua regia or a mixture of KClO_3 and concentrated HCl; one of the tests for mercury consists of reducing the resulting mercuric ion with stannous chloride.

These reactions and properties furnish the basis for the scheme of analysis and, when properly applied, the cations of this group

can be separated thus and identified. The order of introducing the reagents and of conducting the various manipulations is shown in Table XIII.

TABLE XIII

DIAGRAMMATIC OUTLINE OF ANALYSIS OF GROUP I

<i>Solution Contains</i>	<i>Precipitate</i>	<i>Residue</i>	<i>Solution</i>
Ag^+	Treated with <u>AgCl</u>	<u>AgCl</u>	$\text{Ag}(\text{NH}_3)_2^+ + \text{Cl}^-$ (Iden.)
Hg_2^{++}	Treat with <u>Hg_2Cl_2</u> dilute HCl; centrifuge; centrifugate discard	<u>Hg_2Cl_2</u> hot water	NH_4OH
Pb^{++}	<u>PbCl_2</u>	<i>Solution</i> Pb^{++} (Iden.)	<i>Residue</i> <u>HgNH_2Cl</u> + <u>Hg</u> (Iden.)
Iden. Pb (a) add K_2CrO_4 → yellow <u>PbCrO_4</u> (b) add H_2SO_4 → white <u>PbSO_4</u> Iden. Ag by acidifying with HNO_3 → white <u>AgCl</u> Iden. Hg by dissolving black residue with aqua regia, removing Cl_2 and adding SnCl_2 → gray or black <u>Hg_2Cl_2</u> or <u>Hg</u>			

PROCEDURE FOR THE ANALYSIS OF GROUP I

Group Precipitation. If the sample is a simple one for this group only, place a 1-ml. portion in a centrifuge tube, and, if it is acidic, neutralize with dilute ammonia reagent. Then add, dropwise, concentrated HCl, stirring or shaking frequently until precipitation is complete. Centrifuge, remove and discard the centrifugate, and wash with a few drops of water. Again centrifuge. Proceed from here with the separation and detection of lead, silver and mercurous mercury.

If the sample is known to contain members of group II (or subsequent groups as well, as stipulated by the instructor) transfer a 1-ml. portion to a centrifuge tube, being sure to shake the sample well and to include some of the solid which may be present in the sample. The solid may be either (1) hydrolyzed salts of bismuth, antimony and tin or (2) chlorides of group I. Test the solution with litmus, and, if acidic, neutralize it with ammonia solution; disregard any precipitate which may be present or may form upon neutralization. Then add, dropwise, concentrated HCl, shaking or stirring frequently until no further precipitate is seen to form. Centrifuge, and test the centrifugate for complete precipitation. Reserve the centrifugate for the analysis of group II. Wash the residue with 3 drops of water, centrifuge again, and add the washings to the centrifugate for group II.

Proceed from here with the detection of the members of this group.

Detection of Lead. Add 5 drops of water to the residue in the centrifuge tube, heat, stir, centrifuge, remove the supernatant liquid to another tube, place a drop of it on a glass slide, and add a drop of K_2CrO_4 solution. A yellow precipitate of $PbCrO_4$ shows the presence of lead.

To test further for the presence of lead, if in doubt, add a drop of concentrated H_2SO_4 to a drop of the solution, and then dilute with 5 drops of water. A white precipitate will be $PbSO_4$.

The failure to obtain a positive test for lead by the use of either K_2CrO_4 or H_2SO_4 is not conclusive proof that the sample does not contain lead; it may mean that the sample does not contain enough lead to be precipitated as $PbCl_2$ in this group.

Detection of Silver. If lead has been shown to be present, wash the residue with hot water until the washings no longer show a test for this ion. After the complete removal of lead, add 2 drops of concentrated NH_4OH and 2 drops of water, stir thoroughly, warm, and centrifuge. A blackening of the residue on the addition of NH_4OH indicates the presence of mercury. After centrifuging, remove the supernatant liquid to another tube. Withdraw a drop of the solution to a test tube, and acidify with dilute HNO_3 . The appearance of a white precipitate of $AgCl$ on acidification with HNO_3 shows the presence of silver.

Transfer another drop to a spot plate. Add a drop of KCN , then one of dimethylamino benzylidine rhodanine reagent, and acidify with HNO_3 . A red or red-violet color proves the presence of silver.

Detection of Mercury. If a black residue remained in the centrifuge tube after treatment with NH_4OH , wash it with water, add 3 drops of aqua regia, and heat in the water bath. Transfer the solution to a crucible, and continue the gentle heating until chlorine gas no longer is given off; this will be indicated by the disappearance of a yellow color in the solution or by the non-appearance of a blue color on moist starch potassium iodide paper held in the vapors escaping from the crucible. After all the chlorine has been removed, dilute the solution with 5 drops of water. To one portion add several drops of $SnCl_2$. A white or gray precipitate proves the presence of mercury, which was present in the original sample in the mercurous condition.

To confirm this, if necessary, place a drop of diphenyl carbazide solution on the spot plate; add a drop of Na_2CO_3 solution and then

a drop of the chlorine-free solution. A violet or blue color confirms the presence of mercury.

THE THEORY OF PRECIPITATION IN BUFFERED SOLUTIONS

In considering the application of the solubility-product principle in Chapter III, three sets of conditions were enumerated, namely, (1) the precipitation of a single compound, the simplest case involved in the theory of precipitation, (2) fractional precipitation in which two or more compounds are being precipitated from the same solution, such as the precipitation of whole groups of ions and (3) controlled precipitation in buffered solutions in which exact conditions are maintained by common-ion effect. Some examples of the last-mentioned already have been encountered, as, for example, the precipitation of BaCrO_4 in a weakly acid solution, buffered with sodium or ammonium acetate, and the prevention of the precipitation of $\text{Mg}(\text{OH})_2$ in weakly basic (ammoniacal) solutions, buffered with ammonium chloride. These examples will receive more detailed consideration later in this section.

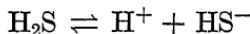
The outstanding classical example of buffered precipitation is the precipitation of sulfides in solutions buffered with HCl, by which the sulfide ion concentration is accurately regulated.

The discussion of controlled precipitation involves a consideration of solubility-product constants, together with ionization constants and common-ion effect.

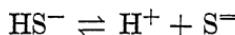
The Theory of the Sulfide Precipitation. If H_2S is passed into neutral solutions containing ions such as Hg^{++} , Cu^{++} , Sn^{++} , Fe^{++} , Zn^{++} , Ni^{++} and Co^{++} , the corresponding sulfides will be formed; some of these sulfides, it is true, will precipitate sooner or more rapidly than others, but eventually all will be precipitated. If, however, the solutions are acidified first with HCl, so that the acidity (H^+ ion concentration) is about 0.3 M , and then H_2S is passed in, only the sulfides of group II will be precipitated. These facts form the basis for the separation of group II from group III. To explain the action of H_2S as a precipitating agent under these conditions, the following must be taken into consideration:

1. The ionization of H_2S .
2. The solubility-product constants of the sulfides of groups II and III.
3. The effect of a common ion on the H_2S equilibrium.
4. Adjustment of the acidity.

1. *The ionization of H₂S.* Hydrogen sulfide is a weakly ionized diprotic acid. It dissolves to some extent in water, forming at room temperature a saturated solution which is 0.1 M with respect to H₂S. It ionizes in two stages, forming first H⁺ ions and hydro-sulfide, HS⁻, ions by its primary ionization:



The hydrosulfide ions further ionize to an extremely slight extent into sulfide ions and hydrogen ions, according to the secondary ionization:



The concentrations of hydrogen ion, hydrosulfide ion and sulfide ion which can exist in equilibrium with dissolved and non-ionized H₂S have been determined by experiment. It has been found that, in a liter of a saturated solution of H₂S in water at 25° C. the concentrations are, respectively, 9.5 × 10⁻⁵ gram ion of hydrogen ion; 9.5 × 10⁻⁵ gram ion of hydrosulfide ion; 1.2 × 10⁻¹⁵ gram ion of sulfide ions and approximately 0.1 gram mole of H₂S.

For the primary ionization we have

$$\frac{C_{\text{H}^+} \times C_{\text{HS}^-}}{C_{\text{H}_2\text{S}}} = K_1$$

or

$$\frac{(9.5 \times 10^{-5}) \times (9.5 \times 10^{-5})}{1 \times 10^{-1}} = 9.0 \times 10^{-8}$$

and, for the secondary ionization,

$$\frac{C_{\text{H}^+} \times C_{\text{S}^=}}{C_{\text{HS}^-}} = K_2$$

or

$$\frac{(9.5 \times 10^{-5}) \times (1.2 \times 10^{-15})}{9.5 \times 10^{-5}} = 1.2 \times 10^{-15}$$

Combining the two ionization equilibria by multiplying K₁ by K₂ gives

$$\frac{(C_{\text{H}^+})^2 \times C_{\text{S}^=}}{C_{\text{H}_2\text{S}}} = K_1 \times K_2 = K_3$$

or

$$\frac{(9.5 \times 10^{-5})^2 \times 1.2 \times 10^{-15}}{1 \times 10^{-1}} = 1.1 \times 10^{-22}$$

K_3 is the over-all ionization constant of H_2S and has the value 1.1×10^{-22} .

Since, however, we are interested mainly in the amount of sulfide ion which is available for the precipitation of sulfides, in a saturated solution of H_2S and in the amount of H^+ ion which can be added at will, it is more convenient to rewrite the preceding expression in the form of the product of the ions by transposing the factor $C_{\text{H}_2\text{S}}$, which is practically constant (0.1 or 1×10^{-1} gram mole). The product of the square of the hydrogen-ion concentration and the sulfide-ion concentration then becomes

$$(C_{\text{H}^+})^2 \times C_{\text{S}^-} = 1.1 \times 10^{-22} \times 1 \times 10^{-1} = 1.1 \times 10^{-23} = K_{\text{H}_2\text{S}}$$

This new constant is designated $K_{\text{H}_2\text{S}}$. Inasmuch as this product represents an equilibrium condition, the value of 1.1×10^{-23} always will be maintained, though the concentration of H^+ ion or S^- ion may be varied at will. If the H^+ ion concentration is increased greatly by the addition of a strong acid, HCl , for example, the S^- ion concentration in equilibrium must decrease greatly; or, if H^+ ions are practically removed by the addition of a base like NH_4OH , the S^- ion concentration will become enormous.

2. *Solubility-Product Constants of Sulfides.* In order for a precipitate of a sulfide to form, the product of the concentration of the cation and that of the sulfide ion must exceed the value of the $K_{\text{s.p.}}$ of the sulfide in question. The data for a number of sulfides are given in Table XIV. Others are given in Table XXVIII.

TABLE XIV

Sulfide	Solubility in Grams per Liter	Solubility in Moles per Liter	Solubility-Product Constant ($K_{\text{s.p.}}$)
HgS	1.5×10^{-24}	6.4×10^{-27}	4.1×10^{-53}
CuS	8.8×10^{-21}	9.2×10^{-23}	8.5×10^{-45}
CdS	8.6×10^{-13}	6.0×10^{-15}	3.6×10^{-29}
PbS	4.9×10^{-12}	2.0×10^{-14}	4.0×10^{-28}
ZnS	3.3×10^{-10}	3.4×10^{-12}	1.2×10^{-23}
FeS	3.4×10^{-8}	3.9×10^{-10}	1.5×10^{-19}
MnS	3.3×10^{-6}	3.8×10^{-8}	1.4×10^{-15}

Knowing that the constants represent solutions saturated with respect to the metallic and sulfide ions, and using such concentrations of metallic ions as are employed in the test solutions, we can maintain a sufficient sulfide-ion concentration from the ionization of H_2S to exceed the value for the respective solubility-product

constants of the cations of both groups II and III. Since the sulfide-ion concentration in a liter of saturated H_2S is 1.2×10^{-15} , a few simple calculations will show this to be true. If we consider a series of test solutions or a mixture of metallic ions in a sample to contain 1 milligram of the respective ions per milliliter (1 gram per liter), the concentrations, in general, will be of the order of 0.01 or 1×10^{-2} gram ion per liter (1 gram divided by the atomic weight). If these values are used in the solubility-product equation,

$$C_{\text{Metallic ion}} \times C_{\text{Sulfide ion}} = K_{\text{s.p.}}$$

in the cases of the divalent metals, the products of the concentrations of the metallic ion and the sulfide ion from H_2S are $1 \times 10^{-2} \times 1.2 \times 10^{-15}$, or uniformly 1.2×10^{-17} . This value exceeds the solubility-product constants for all divalent metals. The following examples will illustrate this.

Example 1. If into 1 ml. of a solution containing 1 milligram of Pb^{++} ion we pass H_2S , will a precipitate of PbS form?

Converting the quantity of Pb^{++} ion to gram-ion concentration (1 milligram per 1 ml. = 1.0 gram per liter) by dividing by the atomic weight of lead, 207.2, gives 4.8×10^{-3} gram ion Pb^{++} per liter. Substituting in the solubility-product equation:

$$C_{\text{Pb}^{++}} \times C_{\text{S}^-} = K_{\text{s.p.}}$$

$$4.8 \times 10^{-3} \times 1.2 \times 10^{-15} = 5.8 \times 10^{-18}$$

shows that the product of the ionic concentrations, 5.8×10^{-18} , greatly exceeds the $K_{\text{s.p.}}$, 4.0×10^{-28} , and therefore PbS will precipitate. The concentrations of Pb^{++} or S^- or both can be even much smaller than in this example for PbS to be precipitated.

Example 2. What is the least sulfide-ion concentration required to start the precipitation of FeS , whose $K_{\text{s.p.}}$ is 1.5×10^{-19} , in a solution containing 0.1 gram ion per liter of Fe^{++} ion?

From the equation,

$$C_{\text{Fe}^{++}} \times C_{\text{S}^-} = K_{\text{s.p.}} \text{ of FeS}$$

$$1 \times 10^{-1} \times x = 1.5 \times 10^{-19}$$

the concentration of S^- needed is 1.5×10^{-18} . This is much less than that ordinarily supplied by H_2S (1.2×10^{-15}).

The extremely small values for the constants for HgS and CuS , for instance, are easily reached and exceeded; whereas, by the

use of test solutions of the same strength for zinc and iron, relatively much greater concentrations of sulfide ion are required for saturation and subsequent precipitation of ZnS and FeS . In order for a division of the sulfides into group II and group III to be made, the sulfide ion must be regulated carefully. This is accomplished by common-ion effect.

If it is desired to cause the precipitation of the metallic sulfides whose $K_{s.p.}$ values are smaller than about 1×10^{-26} and at the same time prevent the precipitation of sulfides whose $K_{s.p.}$ values are greater than this value, it can be seen from the equation,

$$C_{M^{++}} \times C_{S^-} = 1 \times 10^{-26}$$

that, for solutions in which the metallic-ion concentrations are of the order of 10^{-2} gram ion per liter, the sulfide-ion concentration must be reduced from its value, 1.2×10^{-15} , in an ordinary saturated solution of H_2S more than a millionfold. This reduction is brought about by buffering with HCl.

3. Common-Ion Effect. By applying the common-ion effect principle one can calculate readily the decrease in the sulfide-ion concentration through the addition of HCl.

Example 3. Calculate the progressive decrease in sulfide-ion concentration as the H^+ ion concentration is increased progressively to 10^{-3} ; 10^{-2} ; 10^{-1} .

Substituting in the H_2S equilibrium,

$$(C_{H^+})^2 \times C_{S^-} = 1.1 \times 10^{-23}$$

we can see that the sulfide-ion concentration decreases inversely as the square of the H^+ ion concentration and has the values, 1.1×10^{-17} , 1.1×10^{-19} and 1.1×10^{-21} , respectively.

Example 4. In order to maintain a S^- ion concentration of 1.0×10^{-22} , what must be the H^+ ion concentration?

From the equation,

$$(C_{H^+})^2 \times 1.0 \times 10^{-22} = 1.1 \times 10^{-23}$$

the H^+ ion concentration required is $\sqrt{1.1 \times 10^{-1}}$ or 0.317 gram ion per liter.

4. Adjustment of the Acidity. It has been found by experiment and deduced by calculation that, if the acidity of the solution is made 0.3 M with respect to HCl (that is, if enough HCl is added to maintain a hydrogen-ion concentration of 0.3 gram ion per liter),

the sulfides of only group II will be precipitated. By the following calculation of the H_2S equilibrium,

$$(C_{\text{H}^+})^2 \times C_{\text{S}^-} = K_{\text{H}_2\text{S}}$$

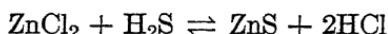
$$(0.3)^2 \times x = 1.1 \times 10^{-23}$$

the sulfide-ion concentration will be reduced to and maintained at 1.2×10^{-22} , if the solution containing metallic ions of group II is made 0.3 M with respect to HCl.

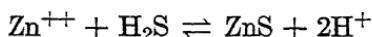
Various expedients are employed for adjusting the solution to the proper acidity. In the macro technique, the addition of 2.5 ml. of concentrated HCl in a total volume of 100 ml. of the solution is the correct amount. In semi-micro technique, where the measurement of the corresponding extremely small volume of acid is impracticable, the use of indicators is resorted to. In the procedure recommended here, methyl orange test paper is employed. This dyestuff indicator has a pink color in solution whose acidity ranges down to about 10^{-4} gram ion of H^+ per liter and an orange color in solutions of still lower acidity. The method of making the adjustment is to dip the platinum wire into the solution, touch it to the test paper, and add dilute HCl or NH_4OH to the solution until the test paper is at the change point of color; then finally add a drop of dilute HCl in excess. This final drop will increase the acidity in 1 ml. of the solution to approximately that required for regulation of the sulfide-ion concentration.

Controlled Precipitation in Acetate-Buffered Solutions. Two examples can be cited in which a controlled precipitation can best be carried out in a weakly acidic solution, buffered with an acetate, namely, the precipitation of ZnS and BaCrO_4 .

As just shown, ZnS cannot be precipitated by H_2S in a solution whose acidity is about 0.3 M or higher with respect to HCl, because the solubility-product constant of ZnS is not exceeded, the S^- ion concentration being too low. From the reaction,



or, ionically,



it readily can be seen that, even if some ZnS forms, the precipitation cannot be complete, because, as the reaction progresses, the concentration of HCl, that is, H^+ ion concentration gradually increases, and before long the acidity will have reached the point where the reaction reverses. From an ionic point of view,

this is better explained by the statement that the increase in H^+ ion concentration represses the S^- ion concentration to such an extent that the $K_{s.p.}$ of ZnS no longer is exceeded. That is, in the ionic reaction,



as the concentration of H^+ ion builds up, the H_2S equilibrium shifts to the left. To prevent the lowering of the S^- ion concentration the solution is buffered by $NaC_2H_3O_2$ or $NH_4C_2H_3O_2$, and the acetate ions unite with the H^+ ions as rapidly as the latter are formed, producing weakly ionized $HC_2H_3O_2$ and satisfying the acetic acid equilibrium. Under these conditions the precipitation of ZnS can be made practically complete.

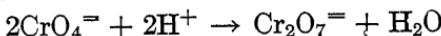
Example 5. In order to maintain a hydrogen-ion concentration of 1×10^{-2} , so that sufficient sulfide ions are available to exceed the $K_{s.p.}$ of ZnS, what gram-ion concentration of $C_2H_3O_2^-$ ion should be supplied to a 0.1 M solution of $HC_2H_3O_2$?

From the equilibrium,

$$\frac{C_{H^+} \times C_{C_2H_3O_2^-}}{C_{HC_2H_3O_2}} = 1.8 \times 10^{-5}$$

since $C_{H^+} = 1 \times 10^{-2}$ and $C_{HC_2H_3O_2}$ is arbitrarily placed at 1×10^{-1} , the $C_{C_2H_3O_2^-}$ is 1.8×10^{-4} gram ion per liter.

In the case of the precipitation of $BaCrO_4$ (see under "Alkaline Earth Elements," page 81), where it is desirable to prevent the simultaneous precipitation of $SrCrO_4$, we have another instance of controlled precipitation. If a solution of a chromate, such as K_2CrO_4 is strongly acidified, the CrO_4^- ion condenses to the dichromate ion,



and this would prevent the formation of $BaCrO_4$ as well as $SrCrO_4$. But if the acidity is correctly controlled, in a dilute solution of $HC_2H_3O_2$ to which $NaC_2H_3O_2$ is added, no appreciable concentration of $Cr_2O_7^-$ ion is present, and at the same time the CrO_4^- ion concentration is sufficiently lowered so that, although the CrO_4^- ion concentration required to reach and exceed the $K_{s.p.}$ of $BaCrO_4$ is maintained, there is not enough CrO_4^- ion to cause the precipitation of $SrCrO_4$.

Controlled Precipitation in Basic Solutions. The important example here is in the prevention of the precipitation of $Mg(OH)_2$ in the ammoniacal solutions from which groups III and IV are precipitated. It will be recalled that, in order to reserve the

identification of magnesium until, in a systematic analysis, group V is reached, NH_4Cl was added to the NH_4OH contained in the group reagents. One can calculate readily from the solubility-product equation,

$$C_{\text{Mg}^{++}} \times (C_{\text{OH}^-})^2 = K_{\text{s.p.}} (3.5 \times 10^{-11})$$

the maximum OH^- ion concentration which can be present in a solution, in the presence of a stipulated Mg^{++} ion concentration, without causing the $K_{\text{s.p.}}$ to be exceeded. Such an OH^- ion concentration would exist in an NH_4OH solution of the strength usually employed. To lower the C_{OH^-} sufficiently, the common-ion effect is utilized, and an ammonium salt, usually NH_4Cl , is added. The necessary $C_{\text{NH}_4^+}$ can be calculated approximately from the NH_4OH equilibrium,

$$\frac{C_{\text{NH}_4^+} \times C_{\text{OH}^-}}{C_{\text{NH}_4\text{OH}}} = 1.75 \times 10^{-5}$$

and, from this, the required weight in grams for the volume of solution under consideration can be determined, to give the proper buffering effect.

Example 6. If you mix 100 grams of NH_4Cl and 50 ml. of concentrated NH_4OH (specific gravity 0.900, containing 28.33 per cent of NH_3 by weight), and dilute to a liter with water, how many grams of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ can be added without $\text{Mg}(\text{OH})_2$ precipitating? $K_{\text{s.p.}}$ of $\text{Mg}(\text{OH})_2$ is 3.5×10^{-11} and K_{ion} of NH_4OH is 1.75×10^{-5} .

First find the OH^- ion concentration which exists in the solution. The concentration of NH_4^+ is $100/53.5$ or 1.87 gram ion per liter. The molarity of the solution with respect to NH_3 (which is also the molarity with respect to NH_4OH) is $50.0 \times 0.900 \times 0.2833/17$ or 0.75.

Solving for x , the OH^- ion concentration, in the equation,

$$\frac{C_{\text{NH}_4^+} \times C_{\text{OH}^-}}{C_{\text{NH}_4\text{OH}}} = 1.75 \times 10^{-5}$$

gives $C_{\text{OH}^-} = 7 \times 10^{-6}$.

From the solubility-product equation,

$$C_{\text{Mg}^{++}} \times (C_{\text{OH}^-})^2 = 3.5 \times 10^{-11}$$

$C_{\text{Mg}^{++}} = 0.72$ gram ion per liter. The weight in grams is then 0.72×203 or 146 grams of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$.

**QUESTIONS AND PROBLEMS—SET 7. BUFFERED
PRECIPITATION**

1. A series of solutions of HCl was saturated with H₂S. The total H⁺ ion concentrations varied as given below. What are the corresponding S⁼ ion concentrations? $(C_{H^+})^2 \times C_{S^=} = 1.1 \times 10^{-23}$

- (a) 1.0
- (b) $1.0 \times 10^{-1.5}$
- (c) 1.0×10^{-3}
- (d) 1.0×10^{-4}
- (e) $1.0 \times 10^{-4.2}$

- Ans.* (a) 1.1×10^{-23}
- (b) 1.1×10^{-20}
- (c) 1.1×10^{-17}
- (d) 1.1×10^{-15}
- (e) $1.1 \times 10^{-14.6}$

2. A liter of solution, saturated solution of H₂S, contained 42.3 ml. of concentrated HCl (specific gravity 1.19, containing 37 per cent HCl). Portions were taken as follows and are diluted to 1 liter. What were the H⁺⁺ ion and S⁼ ion concentrations in each solution? $(C_{H^+})^2 \times C_{S^=} = 1.1 \times 10^{-23}$

- (a) Undiluted
- (b) 100 ml. to a liter
- (c) 10.0 ml. to a liter
- (d) 1.00 ml. to a liter

3. What volumes of concentrated HCl (specific gravity 1.19, 37.23 per cent by weight of HCl, 90 per cent ionized) must be added to liter amounts of solutions saturated with H₂S in order to maintain the following sulfide-ion concentrations:

$$C_{S^=} - \begin{cases} (a) 1 \times 10^{-17} \\ (b) 1 \times 10^{-19} \\ (c) 1 \times 10^{-21} \end{cases}$$

- Ans.* (a) 0.10
- (b) 0.96
- (c) 9.60

4. A liter of a certain solution contained 1.00 ml. of concentrated HCl (specific gravity 1.19, containing 37.23 per cent of HCl) into which H₂S was passed until a volume of 224 ml. of the gas (STP) was absorbed. What were the concentrations of H⁺ and of S⁼ in the resulting solution? At this concentration HCl can be assumed to be completely ionized. Hint: Relate the volume of H₂S to the gram-molecular volume. $\frac{(C_{H^+})^2 \times C_{S^=}}{C_{H_2S}} = 1.1 \times 10^{-22}$

5. By suitable calculations show which of the following solubility constants are exceeded when H₂S is passed into liter solutions containing 0.01 gram ion of the metallic ion and 0.3 gram ion of hydrogen ion. $(C_{H^+})^2 \times C_{S^=} = 1.1 \times 10^{-23}$

Sulfide	$K_{s.p.}$
(a) PbS	4.2×10^{-28}
(b) HgS	4.0×10^{-53}
(c) MnS	1.4×10^{-15}
(d) ZnS	1.2×10^{-23}

- Ans.* Exceeded
- Exceeded
- Not exceeded
- Not exceeded

6. A certain solution contains 0.1 gram ion of Zn⁺⁺ ion per liter and is 0.3 M with respect to HCl (80 per cent ionized). Show by a calculation whether

or not ZnS will be precipitated when H₂S is passed in. $K_{s.p.}$ of ZnS is 1.2×10^{-23} . $(C_{H^+})^2 \times C_{S^-} = 1.1 \times 10^{-23}$

7. In order to prevent the precipitation of FeS when H₂S is passed into a liter of solution containing 0.01 gram ion of Fe⁺⁺ ion, what must be the hydro-gen-ion concentration? $K_{s.p.}$ of FeS is 1.5×10^{-19} . $(C_{H^+})^2 \times C_{S^-} = 1.1 \times 10^{-23}$ *Ans.* 8.5×10^{-4}

8. In 1 ml. of a solution containing 1 milligram of Cd⁺⁺ ion and 0.025 ml. of concentrated HCl (specific gravity 1.19, containing 37.23 per cent by weight of HCl), will CdS be precipitated when H₂S is passed in? Prove your answer by a calculation. $K_{s.p.}$ of CdS is 3.6×10^{-29} . $(C_{H^+})^2 \times C_{S^-} = 1.1 \times 10^{-23}$

9. What volume of concentrated HCl (specific gravity 1.19, containing 37.23 per cent HCl by weight, 80 per cent ionized) is required to repress the ionization of H₂S sufficiently in order that MnS is not precipitated from a liter of solution containing 0.01 gram ion of Mn⁺⁺ ion? $K_{s.p.}$ of MnS is 1×10^{-15} . $(C_{H^+})^2 \times C_{S^-} = 1.1 \times 10^{-23}$ *Ans.* 0.001 ml.

10. Suppose that a divalent metal exists, the solubility-product constant of whose sulfide has the value 1×10^{-25} . Under the conditions of group II precipitation, would this element be included in group II? Prove your answer by suitable calculations.

11. (a) What is the maximum OH⁻ ion concentration which can be present in a liter of solution which contains 0.05 gram ion of Mg⁺⁺ ion in order that Mg(OH)₂ will not be precipitated?

(b) If the solution is 0.1 M with respect to NH₄OH, how much NH₄⁻ must be added to maintain this OH⁻ ion concentration? $K_{s.p.}$ of Mg(OH)₂ is 3.5×10^{-11} . *Ans.* (a) $C_{OH^-} = 2.5 \times 10^{-5}$ (b) 6.9×10^{-2}

12. Show that, if 50 ml. of concentrated NH₄OH (specific gravity 0.9, containing 28.33 per cent of NH₃ by weight) are added to 100 grams of MgCl₂·6H₂O, and the mixture is diluted to 1 liter, Mg(OH)₂ will precipitate in the solution. $K_{s.p.}$ of Mg(OH)₂ is 3.5×10^{-11} , and K_{ion} of NH₄OH is 1.75×10^{-5} .

13. To 100 ml. of solution containing 1×10^{-30} gram ion of Cu⁺⁺ and 1×10^{-19} gram ion of S⁻ ion are added 2 grams of CuSO₄ (completely ionized). Show by suitable calculations whether or not CuS will precipitate. $K_{s.p.}$ of CuS is 8.5×10^{-45} . *Ans.* Will be precipitated

14. In a solution of 2 ml. containing 10 milligrams of Mn⁺⁺ ion per milliliter and 0.1 ml. of concentrated HCl (specific gravity 1.19, containing 37.23 per cent by weight of HCl, will MnS be precipitated when H₂S is passed in? $K_{s.p.}$ of MnS is 1.4×10^{-15} .

15. If a sample of alloy contains 0.25 gram of Mg in a liter, and this is to be prevented during the analysis from precipitating in group III where, let us assume, the solution is made 0.1 M with NH₄OH, so that the OH⁻ ion concentration is 0.001, how much NH₄Cl should be added? K_{ion} of NH₄OH is 1.75×10^{-5} . $K_{s.p.}$ of Mg(OH)₂ is 3.5×10^{-11} . *Ans.* 1.6 grams

16. In making magnesium mixture, calculate the amount of NH₄Cl which must be added to 100 grams of MgCl₂·6H₂O and 50 ml. of concentrated NH₄OH (specific gravity 0.9, containing 28.33 per cent of NH₃ by weight) in order to prevent the precipitation of Mg(OH)₂ in 1 liter of solution. Assume complete ionization of salts involved. $K_{s.p.}$ of Mg(OH)₂ is 3.5×10^{-11} . K_{ion} of NH₄OH is 1.75×10^{-5} .

17. The $K_{s.p.}$ of ZnS is 1.2×10^{-23} and $(C_H)^2 \times C_S = 1.1 \times 10^{-23}$. Calculate the grams of NaC₂H₃O₂ which must be added to a 0.01 M acetic acid solution, in order that ZnS will be precipitated. The concentration of Zn⁺⁺ is 0.001.

Ans. 53.7 grams

18. How many grams of FeSO₄, 75 per cent ionized, must be added to a liter of solution containing 1×10^{-18} gram ion of S⁼, to start the precipitation of FeS? $K_{s.p.}$ of FeS is 1.5×10^{-19} .

19. A solution contains 0.01 gram ion of Cd⁺⁺ ion and Co⁺⁺ ion per liter. Between what limits should the sulfide-ion concentration be maintained if only CdS is to be precipitated?

Ans. 3.6×10^{-27}

3×10^{-24}

20. One tenth of a gram mole of CaC₂O₄ is placed in water, 0.2 gram mole of HCl is added, and the volume brought up to 1 liter with water. What is the resulting gram-ion concentration of calcium? If the H₂C₂O₄ is 40 per cent ionized (primary stage), what is the H⁺ ion concentration of the solution?

THE IONS OF GROUP IIA: MERCURIC ION (Hg⁺⁺), LEAD (Pb⁺⁺), BISMUTH (Bi⁺⁺⁺⁺), COPPER (Cu⁺⁺), CADMIUM (Cd⁺⁺)

The elements whose ions are precipitated by hydrogen sulfide from solutions which are somewhat acidic with HCl (0.3 M) are those which are being studied here in analytical groups I and II. Since, however, in a systematic analysis, silver and mercurous mercury are removed completely as chlorides, and lead is partially so, the elements which exclusively belong to group II are bismuth, copper, cadmium, tin, antimony and arsenic. However, because lead is only partly precipitated as PbCl₂ in group I, and because the mercuric ion (Hg⁺⁺) does not form an insoluble chloride, these two elements must also be included in group II. This group then properly consists of the mercuric and lead ions and the ions of the afore-mentioned 6 elements. The properties of mercury and lead already have been considered; in the present section the reactions of bismuth, copper and cadmium are taken up; the analytical behavior of tin, antimony and arsenic will be considered later.

MERCURIC ION, Hg⁺⁺

Review the properties and preliminary experiments under mercuric mercury in the first part of the chapter.

LEAD, Pb⁺⁺

Review the properties and preliminary experiments under lead in the first part of the chapter.

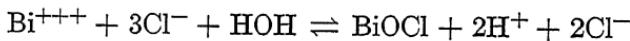
BISMUTH, Bi^{+++}

Bismuth belongs to an important family of elements of which nitrogen, phosphorus, arsenic and antimony are also members. This family is group V of the periodic table. The first two members are distinctly acid-forming, and arsenic is very much so; anions of these 3 elements will be studied later. Antimony and bismuth have properties more like the metallic elements than the acid-forming elements, though they do exist in certain anion forms.

The common valences of bismuth are +3 and +5. The principal oxides are Bi_2O_3 and Bi_2O_5 . The properties and reactions of only the trivalent ion, Bi^{+++} , are considered here. A pentavalent form, in the compound, NaBiO_3 , sodium metabismuthate, already has been encountered as a test reagent for manganese. A characteristic property of bismuth salts is the ease with which they hydrolyze, precipitating insoluble basic salts. Thus the chloride readily hydrolyzes to bismuthyl chloride, better known as bismuth oxychloride, BiOCl ; the nitrate first forms the oxynitrate, BiONO_3 , which then passes over into the subnitrate, $(\text{BiO})_2(\text{OH})\text{NO}_3$. Because of the ease of hydrolysis, the test solution of $\text{Bi}(\text{NO}_3)_3$ is kept strongly acid with HNO_3 to prevent the precipitation of BiONO_3 .

Bismuth hydroxide, $\text{Bi}(\text{OH})_3$, a white solid, is formed when NH_4OH or NaOH is added to a bismuth solution. It is insoluble in an excess of ammonia solution, and differs in this respect from $\text{Cu}(\text{OH})_2$ and $\text{Cd}(\text{OH})_2$, the latter two dissolving to form complex ammono-ions. This property of $\text{Bi}(\text{OH})_3$ serves to separate bismuth from copper and cadmium.

As already noted, solutions of bismuth salts readily react with water; that is, they hydrolyze. In the case of the BiCl_3 , by dilution with water, bismuthyl chloride is precipitated:



This reaction is distinctly reversible, and therefore, if an appreciable amount of acid is added to a solution containing precipitated BiOCl , the latter dissolves. The formation of BiOCl is one of the tests for bismuth.

Bismuth sulfide, Bi_2S_3 , a dark brown very insoluble precipitate, is formed when H_2S or $(\text{NH}_4)_2\text{S}$ is added to a Bi^{+++} solution. This sulfide is insoluble in potassium hydroxide and in cold dilute

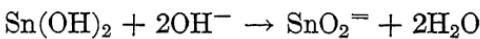
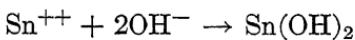
acids, but readily dissolves in hot dilute HNO₃. The reaction can be expressed ionically by the equation:



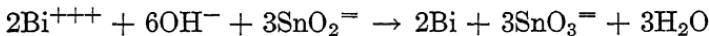
This equation is similar to the one given for PbS; the method of balancing was illustrated on page 178.

Bismuth sulfate, Bi₂(SO₄)₃, is soluble in dilute acid and does not precipitate when sulfuric acid is added to a solution containing bismuth ions (distinction from lead). If, however, the solution is evaporated until the H₂SO₄ becomes quite concentrated, Bi₂(SO₄)₃, insoluble in the concentrated acid, may precipitate.

Sodium stannite reduces Bi⁺⁺⁺ ion or Bi(OH)₃ to black metallic bismuth. This is the best test for bismuth. The reagent is prepared, as needed, by treating a solution of SnCl₂ with an excess of NaOH. In the preparation of this reagent, the product which first forms is Sn(OH)₂, and this dissolves in an excess of the alkali, on account of its amphoteric nature, to form the stannite ion, SnO₂⁼:



When Bi(OH)₃ is treated with this reagent, reduction of the bismuth to the metallic form takes place:



A very sensitive test is the cinchonine-KI reaction. This reagent produces a red precipitate of the type BiI₃·HI cinchonine. The solution to be tested should be only slightly acid. Increase in the acid concentration lowers the sensitivity of the test until finally no reaction is obtained. This test is known as Leger's test. This reaction is not peculiar to cinchonine, since brucine and other alkaloids give similar reactions. In this connection it is interesting to note that bismuth salts commonly are used as reagents for detecting and identifying alkaloids. Cinchonine is an alkaloid derived from quinoline. Other quinoline derivatives such as α - and β -naphthoquinoline and 8-hydroxyquinoline have been suggested as tests for bismuth.

PRELIMINARY EXPERIMENTS

1. Precipitation and Properties of Bismuth Sulfide, Bi_2S_3 . Neutralize 5 drops of $\text{Bi}(\text{NO}_3)_3$ test solution with dilute NH_4OH . Adjust the acidity with dilute HCl , using methyl orange paper, and pass in H_2S . Note the color of the precipitate and write the equation.

Action of Potassium Hydroxide on Bi_2S_3 . Centrifuge the solution, and treat the Bi_2S_3 with a drop of 4 M KOH. Does it dissolve? Compare the action with that for HgS and PbS .

Action of Dilute HNO_3 on Bi_2S_3 . Wash the undissolved precipitate with a small portion of water, centrifuge, then add 5 drops of dilute nitric acid, and heat on the water bath. Show how the equation for the reaction is balanced by supplying the electron equations. Is this property of Bi_2S_3 like that of HgS ? Of PbS ?

2. Action of H_2SO_4 . Add dilute H_2SO_4 to a few drops of bismuth test solution. Does a precipitate of bismuth sulfate form? Compare this with the analogous experiment with lead.

3. Precipitation of $\text{Bi}(\text{OH})_3$. To a few drops of $\text{Bi}(\text{NO}_3)_3$ test solution add dilute NH_4OH until a precipitate forms. Write the equation.

Add an excess of the reagent. Is $\text{Bi}(\text{OH})_3$ soluble in an excess of NH_4OH ?

4. Hydrolysis of Bismuth Chloride. Dissolve a portion of the $\text{Bi}(\text{OH})_3$ obtained in experiment 3 by adding a small amount of dilute HCl , and then dilute the solution with a large volume of water. What forms? What is the equation for the reaction?

5. Sodium Stannite Test for Bismuth. Prepare some sodium stannite reagent by adding a solution of NaOH to a SnCl_2 solution until the $\text{Sn}(\text{OH})_2$ which first forms redissolves. The reagent thus prepared contains the stannite ion, $\text{SnO}_2^{=}$, a good reducing agent. To the remainder of the $\text{Bi}(\text{OH})_3$ obtained in experiment 3 add some of the freshly prepared reagent. What happens? Write the *redox* reaction. This is a very sensitive test for bismuth.

6. Cinchonine-KI Test. To a drop of bismuth test solution on a spot plate add dilute ammonia reagent until basic, and then make very slightly acidic with dilute HCl . Add a drop of cinchonine potassium iodide reagent. What color develops? What is the probable composition of the precipitate?

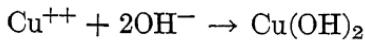
COPPER, Cu^{++}

Copper is one of the most important of metals. It occurs in ores mainly as the sulfide and as basic carbonates. The metal finds wide use in alloys, such as brass and bronze, and as wire and sheet. Some of the salts have technical uses.

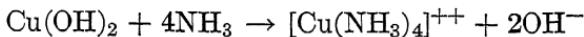
Copper forms two series of salts, the cuprous, in which copper is monovalent, and the cupric, in which the element is divalent. Cuprous salts, which contain the Cu_2^{++} ion, analogous to Hg_2^{++} , are easily oxidized to the cupric form; they are for the most part insoluble in water. The test solution is made from $\text{Cu}(\text{NO}_3)_2$ and hence

contains the cupric ion, Cu⁺⁺. Cupric nitrate is derived by dissolving the black cupric oxide, CuO, in nitric acid.

Cupric hydroxide, Cu(OH)₂, a blue precipitate, is formed when a dilute solution of NaOH or KOH reacts with cupric ion. The same product, or possibly a basic salt, is formed when an equivalent amount of dilute ammonia solution is added to Cu⁺⁺ ions:

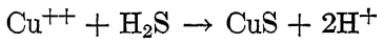


If an excess of the ammonia reagent is used, the precipitate dissolves forming the complex tetrammonocupric ion:



The complex ion has an intensely blue color and is one of the tests for copper.

Cupric sulfide, CuS, is formed when a cupric salt solution is treated with sulfide ions. Cupric sulfide is very insoluble and readily forms when H₂S is passed into a solution of Cu⁺⁺ ions, even if the acidity is high:



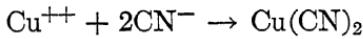
This sulfide is not soluble in potassium hydroxide.

Dilute hot nitric acid dissolves CuS with the formation of Cu⁺⁺, NO, S and water. The equation,

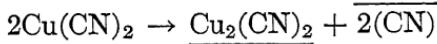


is balanced in the same way as that for the action of HNO₃ on PbS (see page 178).

Cupric ion reacts with an excess of KCN to form a very stable complex. When a cupric solution is treated with KCN, the first result is the formation of cupric cyanide:



This immediately is reduced to cuprous cyanide:

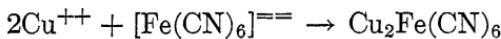


An excess of KCN then reacts and forms a colorless solution which contains the cuprocyanide complex ion:

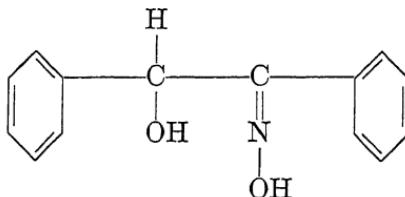


From a solution containing this complex, H_2S will not precipitate Cu_2S . A corresponding but less stable complex is formed with Cd^{++} ion; the difference in stability of these two complexes is utilized to detect cadmium in the presence of copper.

A very sensitive test for copper is the reddish-brown precipitate of cupric ferrocyanide which forms when potassium ferrocyanide is added to a cupric solution:



Benzoinoxime (Cupron) produces a green color with cupric ion. The reagent, sometimes called "Cupron," has the structure:



When a drop is placed on spot paper, treated with a drop of test solution, and held over the ammonia bottle on spot paper to develop the color, a green spot is obtained, owing to the formation of a compound of the chelate type (page 132).

Salicylaldoxime gives a more sensitive and more specific test. When this reagent is used, the test solution is made slightly acid with dilute acetic acid, and the NH_3 development is omitted. Many other oximes, such as formaldoxime, and α -furyl-dioxime, give similar reactions.

PRELIMINARY EXPERIMENTS

1. Precipitation and Properties of Cupric Sulfide, CuS . Place 5 drops of $\text{Cu}(\text{NO}_3)_2$ test solution in a centrifuge tube, adjust the acidity, and saturate the solution with H_2S . Write the reaction. Note the color of the precipitate.

Action of Potassium Hydroxide on CuS . Centrifuge the CuS , and treat a portion of it with KOH, warming the mixture. Is CuS soluble in this reagent to any extent at all?

Action of Dilute HNO_3 on CuS . Treat the remainder of the CuS with hot dilute HNO_3 . Why is an oxidizing solvent necessary to dissolve sulfides like CuS ? In this respect CuS resembles what other sulfides? Show how the equation for the reaction is balanced.

2. Complex Ion of Copper and Ammonia. Add dilute ammonia solution to 5 drops of test solution until a deep blue color develops. What is the complex formed? Name it. Write the equation. Compare the effect here with the action of NH_4OH on AgCl and on $\text{Bi}(\text{OH})_3$.

3. Complex Ion of Copper and Cyanide. To the 5 drops of the Cu(NH₃)₄⁺⁺ solution obtained in experiment 2, add, dropwise, a dilute solution of KCN. *Caution: KCN is a violent poison! Work with extreme care.* Perform the experiment under the hood. Continue adding the reagent until the blue color of the solution is discharged. In what oxidation state is the copper now? Compare the stability of the complex with the corresponding one formed with cadmium. Write the equations, showing the steps in the reactions.

4. Ferrocyanide Test for Copper. Add a few drops of potassium ferrocyanide, K₄Fe(CN)₆, reagent to some of copper test solution. Note the color and give the equation. This is a very sensitive test for copper.

CADMIUM, Cd⁺⁺

This metal is found in association with zinc ores and is recovered during the zinc smelting process. In the periodic table cadmium falls in the same group as mercury and zinc, and, as would be expected, its properties are in many ways similar to those of these two metals. Like mercury, it occurs in both mono- and divalent states, but the monovalent (cadmous) salts are rare and are not considered here.

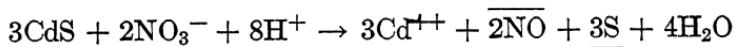
In many of its reactions and salts it resembles zinc; in its behavior toward the analytical reagents of the cation scheme, it closely follows the behavior of copper.

The sulfide and the complexes formed with ammonia and with cyanide ion are the most important forms from an analytical standpoint.

Cadmium sulfide, CdS, yellow, is formed when H₂S is passed into a neutral, alkaline or slightly acid solution of a cadmium salt. If the acidity is somewhat high, precipitation of the sulfide may be incomplete, and there may be formed an orange-colored precipitate of a double salt of the probable composition, CdCl₂·CdS. In slightly acid solutions, the precipitation of CdS is practically complete.

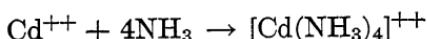
The precipitation of yellow CdS is depended upon as the only practical test for cadmium.

CdS, like the other sulfides of this subgroup, is insoluble in KOH. It dissolves in hot dilute HNO₃,



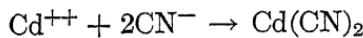
as well as in HCl.

Like the cupric ion, Cd⁺⁺ ion reacts with excess NH₄OH:

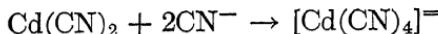


and forms the tetrammonocadmic complex ion corresponding to the tetrammonocupric complex.

The cadmium ion reacts with an equivalent amount of potassium cyanide to form cadmium cyanide:



which is transformed at once by an excess of KCN into the complex cadmium-cyanide ion:



This ion is much less stable than the cuprocyanide complex formed with copper, and this difference in stability enables one to detect cadmium in the presence of copper, for, if H_2S is passed into a solution containing both $[\text{Cu}(\text{CN})_3]^-$ and $[\text{Cd}(\text{CN})_4]^-$, cadmium sulfide only will be precipitated, the great stability of $[\text{Cu}(\text{CN})_3]^-$ suppressing the concentration of cuprous ions to such an extent that Cu_2S cannot form and, by its black color, obscure the yellow color of CdS. See page 371 for the instability constants of these two cyanide complexes.

PRELIMINARY EXPERIMENTS

1. Precipitation and Properties of Cadmium Sulfide, CdS. To 5 drops of $\text{Cd}(\text{NO}_3)_2$ test solution add a drop of dilute HCl, and pass in H_2S . Describe the precipitate that forms.

Repeat the experiment, diluting the mixture to 1 ml. What is the yellow precipitate? Write the equation. From these two experiments state the best conditions for the precipitation of CdS.

Repeat, first adjusting the acidity with HCl, using the methyl orange test paper.

Action of Potassium Hydroxide on CdS. Treat some of the precipitated CdS with KOH, warming the mixture. Does the sulfide dissolve? What other sulfides show a similar behavior?

Action of Dilute HNO_3 on CdS. Treat the remainder of the CdS with dilute HNO_3 , warming if necessary. Show how the equation for the reaction is balanced. What other sulfides already studied show a like behavior toward HNO_3 ?

2. Complex Ion of Cadmium and Ammonia. Neutralize the nitric acid solution obtained in experiment 1 with dilute NH_4OH and then enough of the reagent to dissolve any $\text{Cd}(\text{OH})_2$ which may form. In what form is the cadmium now? Write the equation. Compare this behavior with that for copper.

3. Complex Ion of Cadmium and Cyanide. Add, dropwise, KCN reagent (*caution: violent poison!*) to the solution containing the $\text{Cd}(\text{NH}_3)_4^{++}$ ions until any precipitate which may form redissolves. In what form is the cadmium when an excess of KCN has been added? Write the equations.

Pass H_2S into the solution. What is the yellow precipitate? Explain how KCN and H_2S can be used to identify cadmium in the presence of copper.

REVIEW EXERCISES. CATION GROUP IIA

1. List the formulas and colors of the precipitates encountered in the preliminary experiments of this subgroup.
2. Write the equations for all of the reactions indicated in the diagrammatic scheme for the separation of the ions of this subgroup.
3. Why is Pb^{++} present in this group as well as in group I?
4. Why is mercury included in both groups I and II? Under what conditions will it be found in one group and not in the other?
5. Would it be possible to add mercurous ion to a general unknown and find only mercuric ion? Would it be possible to add mercuric ion to a general unknown and find only mercurous ion? Explain.
6. Which of the metals of group IIA exhibit variable valence? Which of the possible valence states are considered in elementary qualitative analysis?
7. Write a diagrammatic scheme for the separation and identification of the ions in the following mixture: Pb^{++} , Bi^{+++} , Cu^{++} .
8. What single reagent can be used to separate the following pairs of ions: Pb^{++} and Cu^{++} , Bi^{+++} and Cd^{++} , Hg^{++} and Cd^{++} ?
9. A IIA solution yielded a yellow precipitate with H_2S . What ion was known to be present? What ions were known to be absent?
10. A IIA unknown, when made ammoniacal, gave a deep blue color and no precipitate. What ion was known to be present? What ions were known to be absent?

THE IONS OF GROUP IIB: TIN (Sn^{++} , Sn^{++++}), ANTIMONY (Sb^{+++} , Sb^{+5}), ARSENIC (AsO_2^- , $\text{AsO}_4^{=}$)

TIN

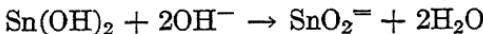
The use of tin by early man in prehistoric times, for the making of weapons and ornaments, ushered in the bronze age. In early times tin was obtained from the British Isles. The present-day deposits are found in Malaya and Bolivia; the mineral is Cassiterite, SnO_2 .

The element exists in two states of oxidation: one, the stannous, in which tin is divalent, and the other, the stannic, in which tin is tetravalent. The compounds of tin may be considered as derived from SnO and SnO_2 , respectively. These oxides are amphoteric and yield salts in which the tin may be present either as cation or as anion as is the case with lead, antimony, arsenic and certain other elements. As might be inferred from its maximum valence, tin, like lead, is in the fourth periodic group.

STANNOUS ION, Sn^{++}

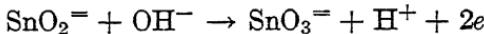
In the divalent state, the simplest form of the ion is the stannous ion, Sn^{++} . However, in solutions such as SnCl_2 , containing a considerable concentration of HCl , the tin probably does not exist as the simple stannous ion, but rather as the chlorostannite, SnCl_4^- ion (or as chlorostannous acid, H_2SnCl_4). Reactions of stannous tin therefore are sometimes written, especially when hydrochloric acid is known to be present, with the SnCl_4^- ion, rather than with the simple Sn^{++} ion.

Stannous hydroxide, $\text{Sn}(\text{OH})_2$ is amphoteric. It forms when NaOH or NH_4OH is added to a SnCl_2 solution and will redissolve in an excess of strong alkali such as NaOH , on account of its amphoteric nature, with the formation of the stannite ion:



It may be recalled that this behavior was involved in the preparation of the sodium stannite reagent employed in the reduction test for bismuth.

The stannite ion is easily oxidized to the stannate ion, the electron equation being:



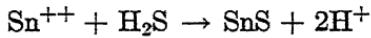
Likewise, the stannous ion is easily oxidized to the stannic state:



Hydrogen peroxide will be employed in the laboratory for this oxidation, the reaction being:



Stannous sulfide, SnS , brown, is precipitated when H_2S is passed into a weakly acidic stannous solution:



This is the only sulfide of group IIB that does not dissolve in KOH reagent. It is, however, soluble in alkali sulfides and polysulfides. Sodium or ammonium polysulfide, for example, will dissolve SnS and, at the same time, oxidize the tin, the final result

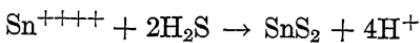
being SnS_3^- , the thiostannate ion. Stannous sulfide is soluble in HCl. Additional properties of the stannous ion are discussed in the following paragraphs.

STANNIC ION, Sn^{++++}

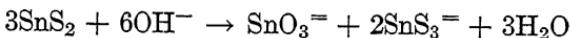
In the stannic state, tin has a valence of +4; a typical compound is SnO_2 . In certain solutions of tetravalent tin, the simple Sn^{++++} ion exists, but in a solution of stannic chloride containing considerable HCl there is probably present SnCl_6^- , the chlorostannate ion.

The hydroxide, $\text{Sn}(\text{OH})_4$, being amphoteric, might as properly be called orthostannic acid. Through the loss of a molecule of water, this is transformed into metastannic acid, H_2SnO_3 , an insoluble compound. It is soluble in HCl forming the chlorostannic ion, SnCl_6^- .

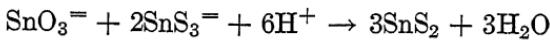
Stannic sulfide is yellow and is formed when a stannic solution is treated with H_2S :



It is soluble in alkaline sulfide reagents as well as in KOH. The latter reagent is used in the scheme of separation employed in this book. When SnS_2 is treated with KOH, there is formed a mixture stannate and thiostannate ions:



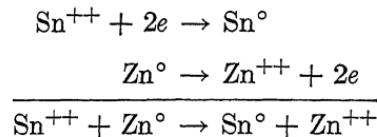
This reaction serves to separate SnS_2 (as well as the sulfides of arsenic and antimony) from the sulfides of division A of this analytical group. When acidified with dilute HCl, the tin in the mixture of these two anions is reprecipitated as SnS_2 :



The readiness with which the ions of tin are oxidized and reduced are important properties of this element. Stannous solutions are strong reducing agents; in this connection, the test for bismuth which uses a solution of sodium stannite should be recalled; in this test Bi^{+++} is reduced to the metallic form, and the stannite ion becomes oxidized to the stannate form.

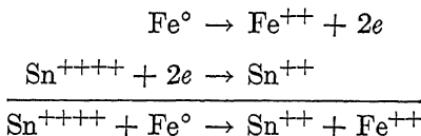
Metals which stand below tin in the electromotive series (see Table XXVI) either will displace tin from its solutions or else will reduce Sn^{++++} to Sn^{++} . Metallic zinc, for example, if placed in a

stannous chloride solution, will reduce the ion to metallic tin. This *redox* reaction may be written thus:



This reaction is sometimes employed as a test for tin.

All the tests for the identification of tin depend upon the properties of the stannous ion; therefore, if the ion is in the stannic condition, it must be reduced before the tests may be applied. This reduction is conveniently effected by making the stannic solution acid with dilute HCl and adding a metal such as iron or magnesium powder. The reaction in the case of iron is balanced by the electron equations:



Mercuric chloride is reduced by SnCl_2 to Hg_2Cl_2 , which is then reduced to Hg. This constitutes one of the tests for tin; it will be recalled that, conversely, this reaction is a test for mercury. The reaction has been discussed under "Mercury," page 175.

The reagent, cacothelin, has been recommended as a test for tin. This test is conducted by placing a drop of the reagent on drop-reaction paper and allowing the paper to dry partially. Then a drop of stannous solution is placed in the center of the spot. A lavender color appears. No other ion of group II will interfere with this test. Care must be taken to employ a fresh solution of the reagent.

The flame-coloration test is perhaps the most distinctive. Details of conducting this test are given under "Preliminary Experiments," page 205.

PRELIMINARY EXPERIMENTS

- Precipitation and Properties of SnS and SnS_2 .** Place 5 drops of SnCl_2 test solution in a centrifuge tube, neutralize with ammonia, adjust the acidity with dilute HCl, and pass in H_2S . Note the color of the precipitate. Write the equation. Centrifuge. Repeat the experiment with 5 drops of SnCl_4 test solution. Note the color of the precipitate. Write the equation. Centrifuge.

To several drops of stannous chloride test solution add several drops of H₂O₂ in order to oxidize the tin. Write the reaction of oxidation of the tin. Neutralize the resulting solution with ammonia, slightly acidify, and pass in H₂S. What is formed?

Action of Potassium Hydroxide on the Sulfides of Tin. Treat the SnS and the SnS₂ with 4 M KOH. Does the SnS dissolve? Does SnS₂ dissolve? In what ionic forms is stannic tin in the solution? Write the equation.

Treat the solution containing the dissolved stannic sulfide with dilute HCl. What is the yellow precipitate which forms? Give the equation for the reprecipitation.

Action of Concentrated HCl on SnS₂. Centrifuge the precipitate obtained in the foregoing experiment, wash thoroughly, and then treat it with concentrated HCl. Compare the action here with the corresponding experiments to be performed with the sulfides of antimony and arsenic.

2. Reduction of Tin Salts. To 2 drops of SnCl₄ solution, acidified with HCl, add a small iron nail. To what is the ion reduced and the iron oxidized? Show this by a *redox* equation. Repeat the experiment, using magnesium powder.

3. Mercuric Chloride Test for Tin. To the stannous chloride solution obtained in experiment 2 add hot HgCl₂ reagent. Note how the color of the precipitate changes as the reagent is gradually added. Give the equations.

4. Flame-Coloration Test. Place about 1 ml. of stannous chloride solution in a small dish; add a small quantity of dilute HCl and a piece of zinc. Place some cold water in a crucible, and, after action of the acid with the test solution has proceeded for some time, pick up the crucible with a pair of tongs, immerse it in the test solution, and then hold it in the practically colorless flame of a burner. Observe that, where the flame impinges upon the lower part of the crucible, there will be an intense blue-colored flame.

ANTIMONY

The element antimony is a member of the important family of periodic group V, which includes also bismuth, arsenic, phosphorus and nitrogen. The important valences of most of these elements are +3 and +5. With increasing atomic weight, from nitrogen to bismuth the basic properties increase with a corresponding decrease in acidic properties. With antimony, as is to be expected, there exist trivalent and pentavalent compounds, some of which are basic and others acidic, giving rise to cation and anion forms. The sulfides are amphoteric.

ANTIMONIOUS ION, Sb⁺⁺⁺; (SbO₂⁻ and SbO₃⁼)

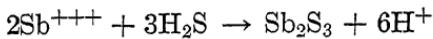
Among the trivalent forms, SbCl₃ and Sb₂S₃ are the most important salts from an analytical standpoint. SbCl₃, when treated with water, readily hydrolyzes to SbOCl:



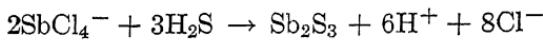
SbOCl is antimonyl chloride, sometimes called antimony oxychloride, and it contains the antimonyl, SbO^+ , ion. The test solution containing the trivalent ion is made by adding sufficient HCl to SbCl_3 to prevent hydrolysis to SbOCl . The antimonyl ion unites with a number of organic anions to form stable organic complexes; for example, with the tartrate ion, complex $[(\text{SbO})\text{C}_4\text{H}_4\text{O}_6^-]^=$ ions are formed, in this way preventing the precipitation of antimony compounds. In a solution of SbCl_3 containing a large amount of concentrated HCl, the antimony probably exists as SbCl_4^- , the chloroantimonite ion.

The Sb^{+++} ion reacts with alkalies to form $\text{Sb}(\text{OH})_3$. This is an amphoteric compound and might be written H_3SbO_3 , ortho-antimonious acid. By the loss of a molecule of water, this is transformed into meta-antimonious acid, HSbO_2 .

Antimonious sulfide, Sb_2S_3 is formed when H_2S is passed into a solution, not too strongly acidic, of trivalent antimony. In the case of the simple ion the reaction is



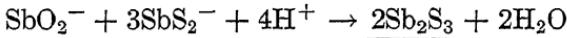
and in solutions acidified with HCl, where the chloroantimonite ion predominates, the reaction is



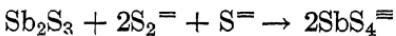
Sb_2S_3 is orange-red in color. It is soluble in alkalies like NH_4OH and KOH, as well as in alkali sulfides and polysulfides. With KOH, the reagent used to divide the sulfides of this group into two subdivisions, there is formed a mixture of meta-antimonite and metathioantimonite ions:



When this solution containing the mixture of SbO_2^- and SbS_2^- ion is acidified with dilute HCl, the trisulfide reprecipitates:

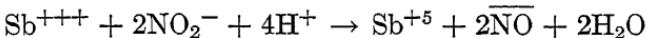


Ordinary ammonium and sodium sulfide dissolve Sb_2S_3 to form the thioantimonite ion, SbS_2^- , but, in the case of the polysulfide reagents, used in some schemes of analysis instead of KOH, the dissolving of antimonious sulfide is accompanied by the oxidation of antimony to the pentavalent state, forming the thioantimonate ion. The reaction can be most simply represented by the equation:

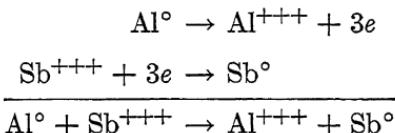


Sb₂S₃ is soluble in concentrated HCl, forming the Sb⁺⁺⁺ ion or possibly the chloroantimonite ion, SbCl₄⁻.

Oxidizing agents, such as KNO₂ and KMnO₄, oxidize the ion to the pentavalent form. In the case of the nitrite, employed in the rhodamine B test, described in the following, the *redox* equation is written



Metals standing above antimony in the electromotive series will reduce the ions of antimony to the metallic condition. The reduction of antimony to the metallic state is a common test for this element. With aluminum, the element forms a black spongy deposit of metallic antimony. This *redox* equation is resolved into:



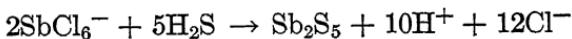
By using a Zn-Pt couple, the deposited metal appears as a black stain on the surface of the bright platinum. The stain is insoluble in sodium hypochlorite. A further confirmatory test is that carried out by using the dyestuff, rhodamine-B. This test is described under "Preliminary Experiments."

ANTIMONIC ION, Sb⁺⁵; (SbO₄⁼)

The important pentavalent compounds of antimony are SbCl₅, Sb₂S₅ and orthoantimonic acid, H₃SbO₄. The latter results when SbCl₅ completely hydrolyzes:



Antimonic sulfide, Sb₂S₅, is formed when H₂S is passed into a solution containing pentavalent antimony ions, provided the solution is not too acidic. When the solution contains much HCl, the chloroantimonate, SbCl₆⁻, predominates over the simple Sb⁺⁵ ion, and hence the precipitation reaction is best written



This sulfide, like Sb₂S₃, is orange-red in color. Like the trivalent sulfide, it is soluble in NH₄OH, KOH and alkali mono- and polysulfides. With KOH, the reaction product is a mixture of the

thioantimonate, SbS_4^{\equiv} and oxyantimonate, SbO_4^{\equiv} . The equation is



Acidification of this solution with dilute HCl results in the reprecipitation of Sb_2S_5 , according to the equation:



The pentavalent sulfide is soluble in concentrated HCl and at the same time is reduced to the trivalent condition, the reaction being accompanied by the evolution of H_2S and formation of sulfur:



The ability of the sulfides of antimony, and of tin as well, to dissolve in concentrated HCl enables them to be separated from arsenic, the sulfides of the latter being insoluble in HCl.

Reducing agents, as, for example, ammonium iodide, reduce antimonic ions to the antimonious form.

PRELIMINARY EXPERIMENTS

1. Precipitation and Properties of Sb_2S_3 and Sb_2S_5 . (a). To 5 drops of SbCl_3 test solution, neutralized with ammonia, add dilute HCl until adjusted with methyl orange paper, and pass in H_2S . Note the color of the sulfide formed, and write the equation. Reserve the precipitate for further experiments.

(b) Repeat the experiment, using a solution of SbCl_5 . What forms? Write the equation.

Action of Potassium Hydroxide on Sb_2S_3 and Sb_2S_5 . Centrifuge the Sb_2S_3 and Sb_2S_5 obtained in experiments 1a and 1b, and treat each with 4 M KOH, warming if necessary to dissolve the precipitates. What has formed? Compare the result with that obtained with the sulfides of tin and arsenic. Write the equations for the reactions.

Add dilute HCl to the solutions just obtained. In what forms is the antimony now? Write the necessary equations.

Add concentrated HCl to the reprecipitated sulfides. Do they dissolve? In what ionic form is the antimony from the Sb_2S_3 ? From the Sb_2S_5 ?

2. Reduction of Antimony Ions. (a). To 2 drops of SbCl_3 test solution add a few pieces of metallic aluminum in the form of chips, turnings or wire. Warm if necessary to start the reaction. What is the black spongy deposit? Explain the action of aluminum.

(b). Repeat the reduction test by placing a small square of sheet platinum in the depression of the spot plate, place on top of this a piece of mossy zinc, cover with dilute HCl, and then add several drops of the test solution. What forms on the bright surface of the platinum? Try the action of NaClO on the black spot; does it dissolve?

3. Rhodamine B Test. The dyestuff, tetraethyl rhodamine, better known as rhodamine B, forms a violet color with pentavalent antimony. To conduct this test the trivalent antimony solution first must be oxidized. Proceed as follows: Place several drops of SbCl_3 test solution in a test tube, and add some crystals of KNO_2 and several drops of concentrated HCl. After effervescence has ceased, add several drops of the dye reagent. A distinct color change from bright red to violet will be observed. Run a blank test in order the better to distinguish the color.

ARSENIC

This is the last of the elements to be studied under the cation procedures. In its reactions it shows a greater variety of properties than do any of the other elements thus far studied. It is mainly an acidic element and in our progressive study makes a natural transition from cation chemistry to the chemistry of the anions.

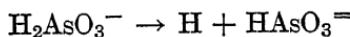
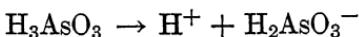
Arsenic forms two series of compounds: the arsenious, in which the element is trivalent, and the arsenic, in which the element is pentavalent. These compounds may be considered as being derived from the two oxides, As_2O_3 and As_2O_5 . Moreover, these oxides are somewhat amphoteric and hence give rise to compounds in which the element may be in either the cation or the anion form. Thus the trivalent forms may be such compounds as AsCl_3 and H_3AsO_3 or HAsO_2 , whereas the pentavalent forms are such compounds as AsCl_5 and H_3AsO_4 .

ARSENIOUS ION, AsO_2^- , As^{+++}

The arsenious test solution supplied in the laboratory contains arsenic in its trivalent forms. It can be prepared by treating As_2O_3 with dilute HCl. Arsenic trioxide dissolves to a limited extent in water, according to the equation:



The product formed, here written as orthoarsenious acid, is an amphoteric substance and also may be assigned the formula $\text{As}(\text{OH})_3$. As a triprotic acid, this substance dissociates in three stages, as shown by the equations:



giving rise to the three anions in decreasing concentrations.

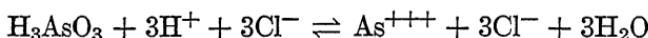
Furthermore, by the loss of a molecule of water from the ortho acid, H_3AsO_3 , there is formed meta-arsenious acid, HAsO_2 :



Meta-arsenious acid is a weak monobasic acid which, by undergoing slight dissociation, produces the meta-arsenite ion:

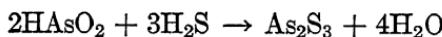


Although these 4 anion forms may exist in an arsenious solution, the undissociated HAsO_2 undoubtedly predominates. Moreover, acidification of an aqueous solution of the oxide increases the solubility of the oxide and promotes the formation of the cation in the form of ionized AsCl_3 .



Since this reaction is reversible, a solution of As_2O_3 dissolved in HCl contains the several anion forms as well as HAsO_2 and As^{+++} , the relative amounts depending on the concentration of the HCl present.

The reactions of arsenic with hydrogen sulfide are extremely important, and the best conditions for the precipitation of the sulfides of arsenic must be understood clearly if trouble is to be avoided. If H_2S is passed into a solution containing arsenic in its trivalent forms, the solution being first acidified with HCl , an immediate and rapid precipitation of yellow arsenious sulfide, As_2S_3 , results. Since the arsenic is present almost entirely in the form of HAsO_2 , the reaction is best shown by the equation:



If the arsenious solution is too weakly acid with HCl , the sulfide will not precipitate and coagulate; instead colloidal As_2S_3 will form and produce a yellow turbidity.

Arsenious sulfide is soluble in alkalis such as KOH , in ammonium hydroxide, and in alkaline sulfides and polysulfides, as well as in nitric acid. It is, therefore, like the sulfides of antimony and SnS_2 , an amphoteric substance. The reaction with hydroxides results in the formation of a mixture of metaarsenite and meta-thioarsenite ions, according to the equation:



This reaction is utilized in the scheme of analysis to dissolve As_2S_3 .

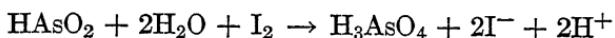
Acidification of these anions with dilute HCl yields As_2S_3 :



Hot concentrated HNO_3 acting on As_2S_3 oxidizes the arsenic to the pentavalent state, forming arsenic acid, and the sulfide ion to free sulfur. The ionic equation is

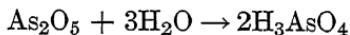


Arsenites are reducing agents and are oxidized by a number of oxidizing substances. The reaction with iodine is an important one, since, as we shall see later in the study of anions, it is employed to distinguish or detect arsenites in the presence of arsenates. The reaction is

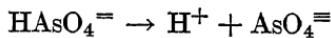
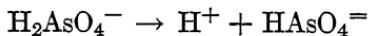
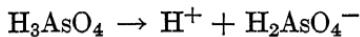


ARSENIC ION, AsO_4^{\equiv} , (As^{+5})

The test solution containing pentavalent arsenic may be made by dissolving arsenic pentoxide in acidified water,



forming arsenic acid, which may, like H_3AsO_3 , undergo ionization in three stages, thus:

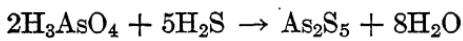


Such a solution consists chiefly of the H_2AsO_4^- ion but contains a certain though small concentration of $\text{HAsO}_4^=$ and a still smaller concentration of the orthoarsenate, AsO_4^{\equiv} , ion.

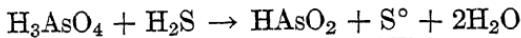
With solutions containing the arsenate (pentavalent) forms, the effect of H_2S is considerably varied, depending upon the conditions of acidity and temperature.

These conditions may be summarized as follows:

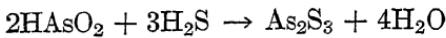
1. If hydrogen sulfide is passed into a cold solution of an arsenate containing a very large excess of concentrated hydrochloric acid, the arsenic is precipitated mainly but slowly as the yellow pentasulfide, As_2S_5 :



2. If, under the same condition of high acidity, the solution is heated and H_2S is passed in, some of the arsenic is precipitated directly as As_2S_5 , but the greater part of it is first reduced by the H_2S to HAsO_2 ,



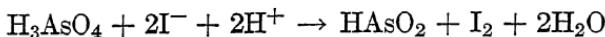
and then precipitated as As_2S_3 ,



and there results a mixture of As_2S_5 , As_2S_3 and S.

3. If the acidity is only moderate and the solution is cold, the arsenate is reduced slowly by the H_2S , and only after a long time will there be formed a precipitate consisting of the trisulfide.

If a reducing agent such as ammonium iodide is added to a moderately acidified solution of an arsenate and then H_2S is passed into the solution, there will be a rapid precipitation of As_2S_3 . The reduction of the arsenate solution by NH_4I may be shown by the equation:

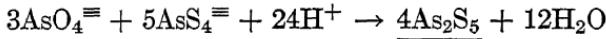


As_2S_5 is soluble in KOH or NH_4OH , as well as in oxidizing acids such as nitric acid and aqua regia. Analogous to Sb_2S_5 , the dissolution with KOH takes place, when an excess of alkali is present, in accordance with the equation,



forming the orthoarsenate and orthothioarsenate ions.

These ions are reprecipitated as As_2S_5 when the solution is acidified with dilute HCl:



Arsenic pentasulfide is also soluble in ammonium or sodium polysulfide, forming the complex thioarsenate ion, $\text{AsS}_4^{=3}$.

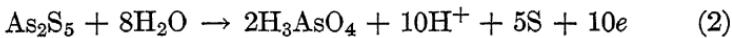
When As_2S_5 dissolves in hot concentrated HNO_3 , the products are H_3AsO_4 , S, NO_2 and water. The balancing of the equation for the action of concentrated HNO_3 on As_2S_5 is accomplished as follows. The nitrate ion is the oxidizing agent and is reduced to NO_2 , requiring one electron for each NO_3^- ion reduced:



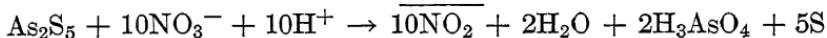
The other electron reaction is the oxidation of the sulfide ion to free sulfur:



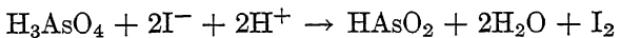
and this, combined with the formation of H_3AsO_4 , which requires 4 oxygen atoms for each atom of arsenic, results in the equation:



Obviously, to balance electrons, equation (1) must be multiplied by 10, and we have



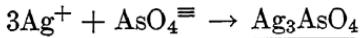
Arsenates act as oxidizing agents toward certain substances as, for example, H_2S , as already shown. The reaction toward the iodide ion,



is, as can be observed readily, the reverse of the reaction of arsenites toward I_2 . In fact, the two equations just given reveal an interesting reversible reaction. The latter equation represents the test for an arsenate in the presence of an arsenite, as conducted in the anion procedure.

For identifying tests for the arsenate ion, as applied in the cation procedure, there are several important reactions. These are:

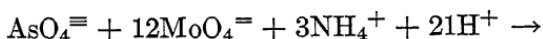
1. Silver nitrate in a neutral solution will precipitate chocolate-colored silver arsenate:



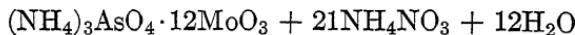
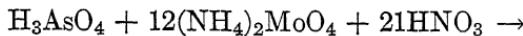
2. Magnesia mixture (a mixture of MgCl_2 and NH_4OH , buffered by NH_4Cl) forms a white crystalline precipitate of magnesium ammonium arsenate:



3. Ammonium molybdate, in a warm nitric acid solution, reacts to form a bright yellow finely divided precipitate known as ammonium arsenomolybdate:



In molecular form this equation is written:



Reactions analogous to (2) and (3) take place with the phosphate ion, but not with the arsenite ion.

4. The Gutzeit test which is described under "Preliminary Experiments."

5. The Bettendorff test, also described under "Preliminary Experiments."

PRELIMINARY EXPERIMENTS

1. **Precipitation and Properties of As_2S_3 and As_2S_5 .** (a). Into 5 drops of arsenite test solution adjusted to the proper acidity with dilute HCl, pass a stream of H_2S . Note the color of the sulfide formed, and write the equation. Note the rapid precipitation of As_2S_3 . Reserve the precipitate for further experiments.

(b) Repeat the experiment, using the arsenate test solution. Is there an immediate precipitate formed? Heat the solution, and again pass in H_2S . What is formed? Write the equations.

(c) Dilute 5 drops of arsenate test solution to 1 ml. with water, add 2 drops ammonium iodide reagent, and acidify with dilute HCl. Show what happens by writing the equation. Then pass H_2S into this reduced solution. What forms? Give the equation.

Action of Potassium Hydroxide on As_2S_3 and As_2S_5 . Centrifuge the As_2S_3 obtained in experiment 1a, treat it with a few drops of 4 M KOH, and stir until solution takes place. In what forms is the arsenic now? Give the equation.

Repeat this part of the experiment with the As_2S_5 . Write the equation for the dissolution of As_2S_5 in KOH.

Acidify the solutions containing the dissolved sulfides with dilute HCl. What are the precipitates which form?

As_2S_3 and As_2S_5 are insoluble in concentrated HCl. Dissolve them by treating with concentrated HNO_3 . Show how the equations are written.

2. **Tests for the Arsenate Ion.** Perform the following experiments, which reveal the properties upon which identifying tests for arsenic are based.

(a) To the solution obtained by dissolving As_2S_5 in nitric acid, add NH_4OH until the solution is neutralized as shown by litmus paper, and then add some silver nitrate reagent. What color is silver arsenate? Write the equation.

(b) To a solution of an arsenate, add an equal volume of magnesia mixture. If precipitation does not result at once, shake the tube vigorously, and set aside for further observation. Describe the precipitate, and give the equation for its formation.

(c) Add dilute HNO_3 to a few milliliters of arsenate test solution, then add ammonium molybdate, and warm, but do not boil. What is the finely divided yellow precipitate? This is an important reaction, and the balancing of the equation should be mastered.

(d) *Gutzzeit Test.* This test gives very satisfactory results on the semi-micro scale. It depends upon the liberation of arsine, AsH_3 , and its subsequent reaction with AgNO_3 . Place a few drops of test solution in a test tube, and add a few granules of zinc (arsenic-free) and a drop or two of dilute H_2SO_4 . Place over the tube a strip of filter paper which has been moistened with a 1:1 solution of AgNO_3 . A yellow or gray spot will form, owing to the formation of the double salt, $\text{AsAg}_3 \cdot \text{AgNO}_3$.

(e) *SnCl_2 (Bettendorff) Test.* Place 2 drops of concentrated HCl on a spot plate, and add 1 drop of arsenic test solution and then 1 or 2 drops of a freshly prepared saturated solution of SnCl_2 in concentrated HCl . A decided brown color forms in one minute or less. The color is due to the reduction to metallic arsenic. The test has been made specific by Feigl by treating a drop of the solution to be tested in a crucible with 1 or 2 drops of NH_4OH , H_2O_2 and saturated MgCl_2 , slowly evaporating and igniting. This treatment converts the arsenic into $\text{MgNH}_4\text{AsO}_4$ and finally into magnesium pyroarsenate $\text{Mg}_2\text{As}_2\text{O}_7$. The ignited residue is treated with the acidified SnCl_2 solution and gently heated, when reduction takes place, forming brownish free arsenic. Many other modifications have been proposed.

REVIEW EXERCISES. CATION GROUP IIB

1. In what valence states can the elements of group IIB exist? Which of these are important in elementary qualitative analysis?
2. Give balanced equations for the reactions involved in the precipitation of sulfides of this subgroup.
3. Give balanced equations showing the dissolving of SnS_2 , Sb_2S_3 , Sb_2S_5 , As_2S_3 and As_2S_5 in KOH ; give the equations for the reactions which take place when the products of these reactions are acidified with dilute HCl .
4. Why is it desirable to have tin present in a sample in the stannic form? Arsenic in the arsenious form?
5. Describe two confirmatory tests for arsenic, antimony and tin.
6. List the oxidizing and reducing agents used in the analysis of IIB. For what specific purpose is each used?
7. Give a diagrammatic scheme for the separation and identification of the following mixture: Sn^{++} , Cu^{++} , Cd^{++} and Sb^{+++} .
8. In a combined group II unknown a yellow precipitate was obtained. Part of the precipitate dissolved in 4 M KOH , and part remained undissolved. What ion was known to be present? What ions may have been present?
9. A group II unknown yielded a black precipitate with H_2S . When a portion was extracted with KOH and the solution was acidified, an orange-colored precipitate was obtained. The black residue was insoluble in HNO_3 . What ions were present?
10. Recall from your general chemistry course the formation of ortho-, meta- and pyro-phosphorous and phosphoric acids from P_2O_3 and P_2O_5 . Following a similar series of reactions, derive the formulas for the corresponding acids of arsenic and antimony, starting with the oxides As_2O_3 and As_2O_5 , Sb_2O_3 and Sb_2O_5 .
11. From their position in the periodic table what would you conclude about the tendency of arsenic and antimony (a) to form positive ions; (b) to form hydroxides which act as acids?

OUTLINE OF THE METHOD OF ANALYSIS OF GROUP II

Membership of This Group. It is first to be noted that mercury, when present in the sample in the mercuric state, properly belongs to this group, being precipitated as HgS . However, since mercurous salts easily are oxidized to the mercuric form, one is apt to find mercury, at least in traces, in this group, even if the original sample contained only mercurous compounds.

Lead, if present in a sample in excess of about 1 milligram per milliliter, will be precipitated partly as PbCl_2 in group I and the remainder as PbS in this group. When smaller quantities are present, all of the lead will be separated and identified in this group.

Bismuth, copper and cadmium constitute the remainder of subdivision A. The ions of tin, antimony and arsenic make up subdivision B.

The separation of this group as a whole into two subgroups is based on the property of stannic sulfide and the sulfides of arsenic and antimony to dissolve in alkalies. A 4 M solution of KOH is used here for this purpose. The ability of these sulfides to react with a base, as well as with strong acids, shows their amphoteric nature. Here their acidic character is utilized. Stannous sulfide, however, is too weakly acidic to dissolve in KOH, and, hence, if tin is present in a sample in the stannous form and is precipitated as SnS , it will escape detection. It is therefore necessary to treat the solution of the sample with an oxidizing agent, in order to convert the tin to the stannic condition. This is done with H_2O_2 . The ideal condition is to have the tin as stannic ion in the original sample.

Arsenic requires special consideration, because it is the most troublesome of all to handle. Arsenic is really an acidic element, and only because it is still basic enough to precipitate as a sulfide with H_2S must provision be made for its precipitation and detection in the cation scheme. In most of the salts of arsenic, the element is present in the anion form, as arsenite if trivalent or as arsenate if pentavalent. The anion scheme provides for the detection both as arsenite and as arsenate. In the lower state of oxidation, as AsO_2^- , it is precipitated rapidly and fairly easily as As_2S_3 from solution with H_2S . In the form of $\text{AsO}_4^{=}$ (or H_2AsO_4^-), the precipitation is slow and incomplete, and special means and precautions must be employed. The ideal condition is to have the arsenic as an arsenite in the original sample for the most satisfac-

tory precipitation. The procedure provides for the reduction of arsenates to the arsenite form by means of NH_4I , and for subsequent precipitation, after SnS_2 and other sulfides have been precipitated.

Group Precipitation. The regulation of the acidity, in order to control the sulfide-ion concentration (1.2×10^{-22} gram ion per liter) so that ions of group III will be prevented from precipitating, has been discussed on page 187. The technique of adjusting the acidity with methyl orange paper also has been described. The detailed procedure describes the method of conducting the group precipitation. If the acidity is improperly adjusted and is too high, CdS , PbS and SnS_2 may be precipitated incompletely or, in cases of gross carelessness, may not be precipitated at all. On the other hand, too low an acidity, that is, too great a sulfide-ion concentration may result in the precipitation and inclusion in this group of ZnS , NiS and CoS . A properly adjusted solution and a correct carrying out of the procedure will result in the precipitation of HgS , PbS , Bi_2S_3 , CuS , CdS , SnS_2 , Sb_2S_3 , Sb_2S_5 , As_2S_3 and possibly As_2S_5 .

Subdivision. By treatment with 4 M KOH these sulfides are subdivided into division A and division B. The effect of KOH is tabulated here:

<i>Subgroup A</i>	<i>Subgroup B</i>
HgS	(HgS_2^{\neq})
PbS	SnS_3^{\neq} and SnO_3^{\neq}
Bi_2S_3	SbS_2^- and SbO_2^-
CuS	SbS_4^{\neq} and SbO_4^{\neq}
CdS	AsS_2^- and AsO_2^- AsS_4^{\neq} and AsO_4^{\neq}

It is to be noted that HgS partially dissolves in the KOH; accordingly, provision is made for the detection of mercury in division B, in case its suspected presence is not proved conclusively in division A.

Separation of the Members of Division A. The successive separation and isolation of the constituents of this subgroup are based on the action of HNO_3 , H_2SO_4 , NH_4OH and KCN as applied in the following steps:

1. Hot dilute HNO_3 will dissolve all of these sulfides except HgS. This must be dissolved in aqua regia or a mixture of KClO_3 and concentrated HCl and the mercury then identified.

2. Lead is separated as PbSO_4 by the action of H_2SO_4 from Bi^{+++} , Cu^{++} and Cd^{++} , and subsequently identified.
3. Ammonia solution will precipitate $\text{Bi}(\text{OH})_3$ and at the same time form $\text{Cu}(\text{NH}_3)_4^{++}$ and $\text{Cd}(\text{NH}_3)_4^{++}$.
4. To detect cadmium in the presence of copper, these ions are converted into the extremely stable complex cyanide, $\text{Cu}(\text{CN})_3^-$ and the less stable $\text{Cd}(\text{CN})_4^-$, from the latter of which CdS can be precipitated.

Identifying tests for the ions of this subgroup are described in the procedure.

Separation of the Members of Division B. 1. The KOH extract containing the thio- and oxy-ions of arsenic, antimony and tin (and possibly HgS_2^-) is acidified with dilute HCl. This reverses the reactions by which the sulfides of this subgroup were dissolved in the alkaline reagent and results in the reprecipitation of As_2S_3 , (As_2S_5) , Sb_2S_3 , Sb_2S_5 , SnS_2 (and possibly HgS).

2. By the action of concentrated HCl, the Sb_2S_3 , Sb_2S_5 and SnS_2 are dissolved, but As_2S_3 and As_2S_5 , as well as HgS , if present, remain as a residue; this furnishes the means of separating antimony and tin from arsenic and mercury. It is to be noted that when concentrated HCl dissolves Sb_2S_5 , the antimony is reduced to the trivalent state.

3. The sulfides of arsenic are soluble in concentrated HNO_3 , by which both sulfides are converted to the $\text{AsO}_4^{=}$ ion. Special provision is made for detecting mercury in this subgroup.

4. No further separation of antimony from tin is necessary, since the recommended identifying tests for each are not interfered with by the presence of the other.

PROCEDURE FOR THE ANALYSIS OF GROUP II

If the sample is one for group II only, transfer 1 ml. to a centrifuge tube, first shaking the sample well and, if the sample contains a precipitate, being sure that some of the suspended precipitate also is transferred. Neutralize the solution with concentrated ammonia, and make slightly acid with dilute HCl.

If the sample is the centrifugate from group I, neutralize it with ammonia, and then make slightly acid with dilute HCl.

In either case, add 5 drops of 3 per cent H_2O_2 to oxidize the stannous tin if it should be present. Heat on the water bath.

TABLE XV
DIAGRAMMATIC OUTLINE OF ANALYSIS OF GROUP II

Precipitate <u>HgS</u>	Residue <u>HgS</u>	Residue <u>HgS</u>	Dissolve in aqua regia, add SnCl_2 —gray or black residue proves Hg.
Pb^{++}	<u>PbS</u>	<u>PbS</u>	Solution <u>Pb⁺⁺</u>
Oxidize with H_2O_2 ; Adjust acid with M.O.;	<u>Bi_2S_3</u>	<u>Bi_2S_3</u>	Heat with dilute HNO_3 . Centrif.
pass in H_2S twice;	<u>CuS</u>	<u>CuS</u>	Bi^{++}
centif. Reduce centif. with NH_4I ; repeat HgS ;	<u>CdS</u>	<u>CdS</u>	<u>Cu^{++}</u>
$\text{AsO}_2^- \equiv \text{AsO}_4^{3-}$	<u>$\frac{\text{As}_2\text{S}_3}{(\text{As}_2\text{S}_3)}$</u>	<u>$\frac{\text{As}_2\text{S}_3}{(\text{As}_2\text{S}_3)}$</u>	<u>Cd^{++}</u>
Sb^{+++}	<u>Sb_2S_3</u>	<u>Sb_2S_3</u>	<u>$\text{Cu}(\text{NH}_3)_4^{++}$</u>
Sb^{+++++}	<u>Sb_2S_6</u>	<u>Sb_2S_6</u>	<u>$\text{Cu}(\text{NH}_3)_4^{++}$</u>
Sn^{++}	<u>SnS_2</u>	<u>SnS_2</u>	<u>$\text{Cu}(\text{NH}_3)_4^{++}$</u>
Sn^{+++++}			<u>$\text{Cu}(\text{NH}_3)_4^{++}$</u>
Residue <u>PbSO_4</u>		Concen- trated H_2SO_4 , evaporate to SO_3 fumes, pour into water. Centrif.	<u>$\text{Bi}(\text{OH})_3$</u>
Residue <u>PbSO_4</u>		Add a slight excess of NH_4OH . Centrif.	<u>$\text{Cu}(\text{NH}_3)_4^{++}$</u>
Residue <u>PbSO_4</u>		<u>Cd^{++}</u>	<u>$\text{Cu}(\text{NH}_3)_4^{++}$</u>
Residue <u>As_2S_3</u>		<u>As_2S_3</u>	<u>$\text{Cu}(\text{NH}_3)_4^{++}$</u>
Residue <u>As_2S_5</u>		<u>As_2S_5</u>	<u>$\text{Cu}(\text{NH}_3)_4^{++}$</u>
Residue <u>Sb_2S_3</u>		<u>Sb^{++}</u>	<u>$\text{Cu}(\text{NH}_3)_4^{++}$</u>
Residue <u>Sb_2S_6</u>		<u>Sb^{++}</u>	<u>$\text{Cu}(\text{NH}_3)_4^{++}$</u>
Residue <u>SnS_2</u>		<u>Sn^{++}</u>	<u>$\text{Cu}(\text{NH}_3)_4^{++}$</u>
<u>Zn-Pt</u>			
<u>NaOCl</u> proves Sb .			
<u>Rhodamine B test</u> .			
<u>(Orange)</u> —Dissolved in HCl ,			
<u>Zn-Pt</u> —black deposit, in-			
<u>soluble in NaOCl proves Sb.</u>			
<u>HgCl_2—white</u>			
<u>precipitate turning black</u>			
<u>proves Sn.</u>			
<u>Flame test.</u>			

Adjustment of Acidity. Concentrate the solution by evaporation until a volume of 1 ml. remains. Adjust the acidity with dilute HCl and NH₄OH, using methyl orange test paper as follows: Dip the platinum wire into the solution, and touch it to the test paper, adding alternately, as required, tiny drops of acid or ammonia solution until the paper is just pink; then add a drop of HCl. Heat the solution nearly to boiling, and pass in a stream of H₂S for 1 minute. Cool, add 10 drops of water, and again pass in H₂S for 1 minute. Centrifuge and test the supernatant liquid for complete precipitation by again passing in H₂S. If further precipitation results, again centrifuge.

If arsenic in the arsenate form is likely to be present in the sample (consult instructor), it must be reduced to the arsenite condition. To carry out this step, dissolve a crystal of NH₄I in 3 drops of water, add this to the centrifugate, warm, and again pass in H₂S. Centrifuge if a precipitate forms, and add the As₂S₃ to the main precipitate.

(If the sample is to be analyzed for group III also, transfer the centrifugate to another tube, and boil the solution in the water bath for several minutes until all the H₂S has been driven out; this can be tested by holding a moistened strip of lead acetate test paper in the escaping vapor; a darkening of the paper indicates the presence of H₂S. Stopper, label, and set aside this solution for group III analysis.)

Separation of Group II Sulfides Into Subgroups A and B. The precipitate may contain HgS, PbS, Bi₂S₃, CuS, CdS, As₂S₃, (As₂S₅), Sb₂S₃, Sb₂S₅ and SnS₂. Wash the group precipitate with 10 drops of water saturated with H₂S and containing a drop of dilute NH₄Cl solution. Centrifuge, and discard the washings.

Now add 10 drops of 4 M KOH to the residue, stir, and heat on water bath for several minutes; centrifuge. The residue may contain all of the PbS, Bi₂S₃, CuS and CdS and most of the HgS; this is division A. The centrifugate may contain arsenic, antimony and tin in the form of the thio- and oxy-ions of these elements, with possibly traces of mercury as HgS₂⁻; this is division B.

Repeat the KOH treatment with 2 drops of the KOH reagent. Heat, centrifuge again, and add the washings to the centrifugate of division B.

ANALYSIS OF DIVISION A OF GROUP II

Separation and Detection of Mercury. Wash the sulfide precipitate with 10 drops of water, in order to remove most of the KOH. Then add 5 drops of dilute HNO₃ and 3 drops of water. Boil carefully in the water bath for several minutes. Centrifuge, and remove the supernatant liquid to a crucible. Repeat the treatment with 2 more drops of acid and 2 of water, and add the centrifugate to that removed in the first treatment. These treatments will have dissolved PbS, Bi₂S₃, CuS and CdS, leaving HgS and some gummy sulfur as residue.

If a black residue remains after the HNO₃ treatment, add several drops of aqua regia, and warm. If the residue dissolves, transfer the solution to another crucible, and heat carefully until all the chlorine gas is driven off; this may be shown by the disappearance of a yellow color in the solution or by the non-appearance of a blue color with potassium iodide starch test paper. After the complete removal of chlorine, add several drops of SnCl₂ to a portion of the solution. A white or gray precipitate indicates the presence of mercury.

To confirm this, if necessary, place a drop of diphenyl carbazide solution on a spot plate; add one drop of Na₂CO₃ solution and then a drop of the solution. A violet or blue color confirms the presence of mercury.

Separation and Detection of Lead. Add 5 drops of concentrated H₂SO₄ to the solution in the crucible from the separation of HgS. Boil carefully in the hood until dense white fumes of SO₃ appear. Draw up the liquid from the crucible with a pipet, and allow it to drop slowly into a centrifuge tube containing 10 drops of water. Centrifuge, and, if a white precipitate forms, it is probably PbSO₄. Remove the centrifugate to another centrifuge tube; this may contain Bi⁺⁺⁺, Cu⁺⁺ and Cd.⁺⁺

The white precipitate may contain (BiO)₂SO₄; therefore confirmatory tests for lead should be made.

Wash the residue of PbSO₄ with 2 drops of water, centrifuge, and add the washings to the preceding solution. Now add 2 drops of NH₄C₂H₃O₂ to the white residue, and heat carefully in the water bath. Stir occasionally. After the residue has dissolved, add a drop of dilute HC₂H₃O₂ and a drop of K₂CrO₄ reagent to 3 drops of the solution. A yellow precipitate of PbCrO₄ shows the presence of lead.

Separation and Detection of Bismuth. Very carefully add concentrated NH_4OH to the solution from which the lead has been removed until the solution is alkaline. A white precipitate forming at this time is probably $\text{Bi}(\text{OH})_3$. Continue addition of NH_4OH , stirring, until the solution is definitely basic. If an appreciable amount of copper is present, the solution will become blue at this point.

Centrifuge, remove the liquid, and place it in a test tube or centrifuge tube. Wash the residue with 2 or 3 drops of dilute NH_4OH and 2 or 3 drops of water. Centrifuge, and add the washings to the liquid which may contain copper and cadmium in the form of $\text{Cu}(\text{NH}_3)_4^{++}$ and $\text{Cd}(\text{NH}_3)_4^{++}$ ions.

Remove a small portion of the $\text{Bi}(\text{OH})_3$ precipitate by introducing a small strip of filter paper attached to a platinum wire. Dip the paper into a solution of sodium stannite (Na_2SnO_2) made by adding NaOH to SnCl_2 on a spot plate, until the precipitate which first forms disappears. A blackening of the paper indicates bismuth.

A confirmatory test for bismuth may be made by first dissolving the remainder of the $\text{Bi}(\text{OH})_3$ in a few drops of dilute HCl and then adding 2 or 3 drops of cinchonine potassium iodide reagent; the formation of a red precipitate is proof that bismuth is present.

Detection of Copper. The formation, during the separation of bismuth, of a deep blue solution, which contains the complex copper-ammonia ion, shows the presence of copper. However, if no blue color is observed, the solution should be tested for copper by more sensitive methods. Proceed as follows:

Remove several drops of the solution to a spot plate, acidify with dilute HCl, and add a drop of $\text{K}_4\text{Fe}(\text{CN})_6$ solution. A red precipitate of $\text{Cu}_2\text{Fe}(\text{CN})_6$ proves the presence of copper.

Place another drop of the solution on drop-reaction paper, add a drop of alcoholic α -benzoinoxime and hold the spot near the mouth of the concentrated NH_4OH reagent bottle, in order to develop the color. In the presence of copper, a green coloration will be obtained.

Separation and Detection of Cadmium. In the absence of copper, a simple identifying test for cadmium may be carried out by neutralizing, with dilute H_2SO_4 , a portion of the solution obtained from the bismuth separation, and then passing in H_2S , which will produce a yellow precipitate of CdS if cadmium is present.

In the presence of copper, a separation of cadmium from copper must be resorted to, and for this the cyanide separation is recommended. Add to the solution 5 drops of KCN solution (*extreme caution! deadly poison!*), or enough to discharge the blue color, and then pass in H_2S . A yellow precipitate of CdS shows the presence of cadmium.

ANALYSIS OF DIVISION B OF GROUP II

Carefully add dilute HCl to the KOH solution obtained in the process of subdivision of this group until it is just acidic. The dilute acid will reprecipitate As_2S_3 , (As_2S_5) , Sb_2S_3 , Sb_2S_5 and SnS_2 . Centrifuge; remove, and discard the supernatant liquid. Add 5 drops of concentrated HCl to the residue, heat for 5 minutes, stirring occasionally. Pass in H_2S for 1 minute. Centrifuge, and remove the liquid to a test tube; this solution may contain antimony, as Sb^{+++} or $SbCl_4^-$, and tin, as Sn^{++++} or $SnCl_6^-$. The residue may consist of HgS , As_2S_3 (As_2S_5) and S.

Separation and Detection of Mercury. Treat the residue with 2 drops of dilute HCl and 2 drops of water, and add the washings to the antimony-tin solution. Repeat the washing. Then add 10 drops of dilute NH_4OH to the residue, stir, heat on water bath, centrifuge, and transfer the supernatant liquid to a centrifuge tube. Wash the residue with several more drops of NH_4OH . Complete extraction may be tested for by acidifying a drop of the NH_4OH extract with dilute HCl; a yellow precipitate will appear if arsenic sulfides have not been completely extracted.

If a black residue remains from the NH_4OH treatment, add 2 drops of aqua regia, and warm until dissolved. If the residue appears gummy, it is probably merely sulfur. Test for mercury as described in division A.

Detection of Arsenic. Add dilute HNO_3 to the NH_4OH solution until it is acid, centrifuge, remove, and discard the supernatant liquid. A yellow precipitate at this point is a good indication of arsenic; it is As_2S_3 or As_2S_5 , or a mixture of both. Dissolve by adding 5 drops of concentrated HNO_3 and heating the mixture in the water bath. This action now has converted the arsenic to the $AsO_4^{=}$ ion. Two of the several possible tests for arsenic are here recommended.

1. *The Gutzeit test.* This test is conducted as follows: Transfer a portion of the arsenate solution to another tube; add a few gran-

ANALYSIS OF GROUP II

TABLE XVI
BEHAVIOR OF CATIONS TOWARD CERTAIN REAGENTS

Cation	Dilute HCl	H_2S (H_2O)	$(NH_4)_2S$	$(NH_4)_2CO_3$		NH_4OH		$NaOH$ or KOH	
				Equiv. Amount	Excess	Equiv. Amount	Excess	Equiv. Amount	Excess
Ag ⁺	AgCl white	Ag ₂ S black	Ag ₂ S black	$\frac{Ag_2CO_3}{sol.}$ white	$Ag(NH_4)_2^+$ insol.	$\frac{Ag_2O}{sol.}$ brown	$Ag(NH_3)_2^+$ insol.	Ag_2O brown	insol.
Hg ₂ ⁺⁺	Hg ₂ Cl ₂ white	Hg ₂ S black	Hg ₂ Cl ₂ + Hg white black	$\frac{HgNH_4Cl}{sol.}$ white	$HgNH_4Cl + \frac{Hg}{black}$ black	$\frac{Hg(OH)_2}{sol.}$ white	$\frac{Hg(OH)_2}{sol.}$ white	$\frac{Hg(OH)_2}{sol.}$ white	insol.
Pb ⁺⁺	PbCl ₂ white	PbS black	PbCO ₃ · Pb(OH) ₂ white	PbCO ₃ · Pb(OH) ₂ white	insol.	Pb(OH) ₂ white	insol.	PbO ₂ white	insol.
Hg ⁺⁺	HgS black	HgCO ₃ · (HgO) ₃ brown	HgCO ₃ · (HgO) ₃ brown	insol.	$\frac{HgNH_4Cl}{sol.}$ white	insol.	$\frac{HgO}{sol.}$ yellow	insol.
Bi ⁺⁺⁺	Bi ₂ S ₃ black	Bi ₂ O ₃ · CO ₃ white	Bi ₂ O ₃ · CO ₃ white	insol.	Bi(OH) ₄ white	insol.	Bi(OH) ₃ white	insol.
Cu ⁺⁺	CuS black	CuCO ₃ blue	CuCO ₃ blue	insol.	$\frac{Cu(OH)_2}{sol.}$ blue	$\frac{Cu(OH)_2}{sol.}$ deep blue	$\frac{Cu(OH)_2}{sol.}$ blue	insol.
Cd ⁺⁺	CdS yellow	CdCO ₃ white	CdCO ₃ white	$\frac{Cd(OH)_2}{sol.}$ white	$\frac{Cd(NH_3)_4^{++}}{colorless}$ colorless	$\frac{Cd(OH)_2}{sol.}$ white	insol.
(AsO ₂) ⁻	As ₂ S ₃ yellow sol. in excess	As ₂ S ₃	As ₂ S ₃
Sb ⁺⁺⁺	Sb ₂ S ₃ orange sol. in excess	Sb ₂ S ₃ white	Sb ₂ S ₃ white	insol.	Sb(OH) ₃ white	insol.	Sb(OH) ₃ white	sol.
Sn ⁺⁺	SnS brown sol. in excess	SnS white	SnS white	insol.	Sn(OH) ₂ white	insol.	Sn(OH) ₂ white	SnO_2^- insol.
Sn ⁺⁺⁺	SnS ₂ yellow sol. in excess	SnS ₂ white	SnS ₂ white	insol.	Sn(OH) ₄ white	insol.	Sn(OH) ₄ white	SnO_3^-

ules of zinc and a drop or two of dilute H_2SO_4 . Insert a plug of cotton saturated with lead acetate solution near the mouth of the tube. Place over the tube a strip of filter paper which has been moistened with a 1:1 solution of $AgNO_3$. A yellow or gray spot will form, owing to the formation of the double salt, $AsAg_3 \cdot AgNO_3$.

2. The $AgNO_3$ test. To the remainder of the arsenate solution, add several drops of dilute $AgNO_3$ solution; shake and centrifuge to remove any white $AgCl$ which may form. Add to the centrifugate a little Na_2CO_3 , and shake or stir. A brown precipitate of Ag_3AsO_4 proves the presence of arsenic.

Detection of Antimony. The tests for antimony and tin are made in the antimony-tin solution without further separation. To test for antimony, place a drop of the solution on a spot plate, and add some crystals of KNO_2 and 1 or 2 drops of dilute HCl . When effervescence has ceased, add a drop of rhodamine B reagent. A change in color from bright red to violet shows the presence of antimony. A blank test should be made at the same time.

To identify antimony further, place a small piece of platinum and a piece of zinc in a depression of the spot plate. To this add a few drops of the solution, previously warmed. A black spongy deposit is due to metallic antimony.

Detection of Tin. Reduce the tin in the remainder of the solution to the stannous state by adding some magnesium powder.

Place several drops of the reduced solution on the spot plate, and add some granules of zinc. Immerse the bottom of a crucible in this liquid, and then hold it in the flame of a burner. A bluish flame playing on the surface of the unglazed crucible bottom shows the presence of tin.

To another drop of the reduced solution, add, dropwise, $HgCl_2$ reagent. A white or gray precipitate confirms the presence of tin.

PART II. THE ANIONS

CHAPTER VI

THE CLASSIFICATION OF THE ANIONS. THE ANIONS OF GROUP I. THE *pH* VALUE OF SOLUTIONS

This part of the text deals primarily with the properties, reactions and identification of the anions. Since many of the anions are derived from salts of weakly ionized acids, the important theory of hydrolysis and the closely related concept of the *pH* value of solutions find here an appropriate place for study and correlation. Furthermore, since most of the anions to be studied are either oxidizing or reducing in their properties, a further study of oxidation and reduction, beyond the elementary theory given in Chapter IV, is presented in Chapter IX, in which the electrochemical theory of oxidation and oxidation and oxidation potentials are discussed.

THE CLASSIFICATION OF THE ANIONS

The anions are the negatively charged atoms or groups of atoms, sometimes called "acid radicals." Of those included in this course only 5 are simple ions, namely, the negatively charged atoms of the halogens and of sulfur, yielding the F^- , Cl^- , Br^- , I^- and $S^=$ ions. The remainder are composed of 2 or more elements, ranging in complexity from the relatively simple very stable oxy-ions to the truly complex ions, like those discussed in Chapter IV under the theory of complex ions.

The laboratory work on the cations has familiarized the student with some general and specific properties of practically all of the common anions. They were encountered either as anion forms of the metallic elements or met with as components of a variety of reagents. In the first category are the anions of amphoteric compounds yielding ions such as the unstable ZnO_2^- , $AlO_3^=$ and AlO_2^- ; $CrO_3^=$ and CrO_2^- ; SnO_2^- and SnO_3^- ; PbO_2^- and PbO_3^- ;

TABLE XVII
PERIODIC CLASSIFICATION OF ANIONS

as well as the more stable ions, such as the $\text{AsO}_3^{=}$, AsO_2^- and $\text{AsO}_4^{=}$; SbO_2^- and $\text{SbO}_4^{=}$; BiO_3^- , MnO_4^- , CrO_4^- . Among the reagents employed for precipitating, dissolving, oxidizing, reducing, neutralizing or other purposes were many anions: for example, the Cl^- , S^- and $\text{CO}_3^=$ ion, as group precipitating reagents; many others, such as the ClO_3^- , NO_2^- , NO_3^- , BiO_3^- , $\text{S}_2\text{O}_8^{=}$ used as oxidizers.

To give a better understanding of the relationships between the common anions and between the elements which constitute the parent acids, Table XVII is arranged like the periodic table of the elements and includes only the most important anions of the elements to be studied. If the unstable anions of amphoteric hydroxides and oxides are eliminated, it may be noted that, actually, the common more important anions, for whose detection provision is made in the procedures here, are derived from only a dozen typically acid-forming elements. These are listed here, together with the anions (a total of 25) derived from them, for which provision is made for their detection:

Boron: BO_2^- , $(\text{BO}_3^{=})$, $(\text{B}_4\text{O}_7^{=})$

Carbon: $\text{CO}_3^{=}$, $\text{C}_2\text{O}_4^{=}$, $\text{C}_4\text{H}_4\text{O}_6^{=}$, $\text{C}_2\text{H}_3\text{O}_2^-$, CN^- , SCN^- , $[\text{Fe}(\text{CN})_6]^{=}$, $[\text{Fe}(\text{CN})_6]^{=}$

Silicon: SiO_3^-

Nitrogen: NO_2^- , NO_3^- (SCN^-)

Phosphorus: $\text{PO}_4^{=}$

Arsenic: AsO_2^- , $\text{AsO}_4^{=}$

Sulfur: $\text{S}^{=}$, $\text{SO}_3^{=}$, $\text{SO}_4^{=}$, $\text{S}_2\text{O}_3^{=}$ (SCN^-)

Chromium: $\text{CrO}_4^{=}$ ($\text{Cr}_2\text{O}_7^{=}$)

Fluorine: F^-

Chlorine: Cl^- , ClO_3^-

Bromine: Br^-

Iodine: I^-

The Analytical Grouping of the Anions. Within the last few years several systematic anion schemes have been published. The one employed here, with certain modifications, is that by Dobbins and Ljung. In this procedure, the solution is kept rather strongly basic, for the reason that many reactions between oxidizing and reducing agents do not take place, or take place only to a negligible extent, in a basic solution. The group reagents in succession are $\text{Ca}(\text{NO}_3)_2$, $\text{Ba}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2$ and AgNO_3 , thus dividing the anions into 4 precipitated groups and a soluble group. The group precipitations are outlined here. The basis of the grouping will be evident from the following considerations.

TABLE XVII
DIAGRAMMATIC GROUPING OF THE ANIONS

$\text{CO}_3^{=}$	$\frac{\text{CaCO}_3}{\text{CaC}_2\text{O}_4}$	Group I
$\text{C}_2\text{O}_4^{=}$	$\frac{\text{CaF}_2}{\text{Ca}(\text{BO}_2)_2}$	
F^-	$\frac{\text{CaSO}_3}{\text{Ca}(\text{AsO}_2)_2}$	
BO_2^-	$\frac{\text{Ca}_3(\text{AsO}_4)_2}{\text{Ca}_3(\text{PO}_4)_2}$	
SO_3^-	$\frac{\text{Ca}_3(\text{AsO}_4)_2}{\text{Ca}_3(\text{PO}_4)_2}$	
AsO_2^-	$\frac{\text{CaC}_4\text{H}_4\text{O}_6}{\text{CaSiO}_3}$	
$\text{AsO}_4^{=}$	$\frac{\text{BaSO}_4}{\text{BaClO}_4}$	
$\text{PO}_4^{=}$	$\frac{\text{S}^-}{\text{CN}^-}$	
$\text{C}_4\text{H}_4\text{O}_6^{=}$	$\frac{\text{Fe}(\text{CN})_6^{=}}$	
SiO_3^-	$\frac{\text{Fe}(\text{CN})_6^{=}}$	
$\text{SO}_4^{=}$	$\frac{\text{Fe}(\text{CN})_6^{=}}$	
$\text{CrO}_4^{=}$	$\frac{\text{Fe}(\text{CN})_6^{=}}$	
S^-	$\frac{\text{S}_2\text{O}_3^{=}}$	
CN^-	$\frac{\text{S}_2\text{O}_3^{=}}$	
$\text{Fe}(\text{CN})_6^{=}$	$\frac{\text{SCN}^-}{\text{I}^-}$	
$\text{Fe}(\text{CN})_6^{=}$	$\frac{\text{Ba}(\text{NO}_3)_2}{\text{Br}^-}$	
$\text{S}_2\text{O}_3^{=}$	$\frac{\text{Br}^-}{\text{Cl}^-}$	
SCN^-	$\frac{\text{Cl}^-}{\text{ClO}_3^-}$	
I^-	$\frac{\text{ClO}_3^-}{\text{C}_2\text{H}_3\text{O}_2^-}$	
Br^-	$\frac{\text{C}_2\text{H}_3\text{O}_2^-}{\text{NO}_2^-}$	
Cl^-	$\frac{\text{NO}_2^-}{\text{NO}_3^-}$	
ClO_3^-	$\frac{\text{AgNO}_3}{\text{Zn}(\text{NO}_3)_2}$	Group II
$\text{C}_2\text{H}_3\text{O}_2^-$	$\frac{\text{AgNO}_3}{\text{Zn}(\text{CN})_2}$	
NO_2^-	$\frac{\text{AgNO}_3}{\text{Zn}_2\text{Fe}(\text{CN})_6}$	
NO_3^-	$\frac{\text{AgNO}_3}{\text{Zn}_3[\text{Fe}(\text{CN})_6]_2}$	
ZnS	$\frac{\text{AgS}}{\text{AgSCN}}$	Group III
$\text{Zn}(\text{CN})_2$	$\frac{\text{AgI}}{\text{AgI}}$	
$\text{Zn}_2\text{Fe}(\text{CN})_6$	$\frac{\text{AgBr}}{\text{AgBr}}$	
$\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$	$\frac{\text{AgNO}_3}{\text{AgNO}_3}$	
AgS	$\frac{\text{AgSCN}}{\text{AgSCN}}$	Group IV
AgI	$\frac{\text{AgI}}{\text{AgI}}$	
AgBr	$\frac{\text{AgNO}_3}{\text{AgNO}_3}$	
AgNO_3	$\frac{\text{AgNO}_3}{\text{AgNO}_3}$	
ClO_3^-	$\frac{\text{C}_2\text{H}_3\text{O}_2^-}{\text{C}_2\text{H}_3\text{O}_2^-}$	Group V
$\text{C}_2\text{H}_3\text{O}_2^-$	$\frac{\text{NO}_2^-}{\text{NO}_2^-}$	
NO_2^-	$\frac{\text{NO}_3^-}{\text{NO}_3^-}$	
NO_3^-	$\frac{\text{NO}_3^-}{\text{NO}_3^-}$	

When a mixture of anions, in a solution kept basic with $\text{Ca}(\text{OH})_2$, is treated, successively, with the anion group reagents, the following group precipitations take place:

1. If $\text{Ca}(\text{NO}_3)_2$ reagent is added to the mixture, there will be precipitated calcium carbonate, CaCO_3 ; calcium oxalate, CaC_2O_4 ; calcium metaborate, $\text{Ca}(\text{BO}_2)_2$; calcium sulfite, CaSO_3 ; calcium arsenite, $\text{Ca}(\text{AsO}_2)_2$; calcium arsenate, $\text{Ca}_3(\text{AsO}_4)_2$; calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$; calcium tartrate, $\text{CaC}_4\text{H}_4\text{O}_6$; calcium fluoride, CaF_2 ; and calcium silicate, for which the simplest formula is CaSiO_3 . This group of calcium salts is group I. The supernatant liquid will contain all other anions of which the mixture is composed.

2. If to this supernatant liquid is next added $\text{Ba}(\text{NO}_3)_2$ reagent, barium sulfate, BaSO_4 and barium chromate, BaCrO_4 , will form. This then is group II.

3. $\text{Zn}(\text{NO}_3)_2$ is the reagent for group III and will precipitate zinc sulfide, ZnS ; zinc cyanide, $\text{Zn}(\text{CN})_2$; zinc ferrocyanide, $\text{Zn}_2\text{Fe}(\text{CN})_6$; and zinc ferricyanide, $\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$.

4. With the insoluble calcium, barium and zinc salts successfully removed, if now AgNO_3 reagent is added, there will be precipitated silver thiosulfate, $\text{Ag}_2\text{S}_2\text{O}_3$; silver thiocyanate, AgSCN ; silver iodide, AgI ; silver bromide, AgBr ; and silver chloride, AgCl . This is group IV.

5. There remain, unprecipitated by the group reagents, the chlorate, ClO_3^- ; the acetate, $\text{C}_2\text{H}_3\text{O}_2^-$; the nitrite, NO_2^- , and the nitrate, NO_3^- , ion. These may be considered group V, the soluble anion group.

The properties, reactions and tests for the anions are described in the following sections. In the systematic analysis of mixtures the test for nitrates must be made on a separate portion of the original mixture, because the nitrate ion will have been introduced through the addition of the group reagents.

GROUP I. THE CALCIUM NITRATE GROUP: CARBONATE ($\text{CO}_3^{=}$), OXALATE ($\text{C}_2\text{O}_4^{=}$), FLUORIDE (F^-), TARTRATE ($\text{C}_4\text{H}_4\text{O}_6^{=}$), METABORATE (BO_2^-), SULFITE ($\text{SO}_3^{=}$), ARSENITE (AsO_2^-), ARSENATE ($\text{AsO}_4^{=}$), PHOSPHATE ($\text{PO}_4^{=}$), SILICATE (SiO_3^-)

This group of anions is characterized by the insolubility of their calcium salts. The group precipitating reagent is $\text{Ca}(\text{NO}_3)_2$. In systematic analysis the addition of this reagent to an alkaline solu-

tion of the sample will result in the precipitation of the calcium salts of the anions of this group; all other anions will remain in solution.

CARBONATE, $\text{CO}_3^=$

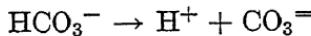
Carbonates are rather widely distributed in nature, in rocks and ores, especially as limestones and dolomites and as many other carbonate minerals. Carbon dioxide is formed in the atmosphere as the product of the oxidation of carbonaceous material. Carbonates and bicarbonates are derived from carbonic acid. When carbon dioxide dissolves in water, carbonic acid is formed, in accordance with the equation:



The amount of H_2CO_3 formed is very small, and the resulting solution is very dilute with respect to the acid. Carbonic acid is a weakly ionized acid, which dissociates in two stages, namely,

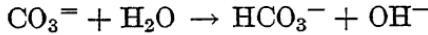


and

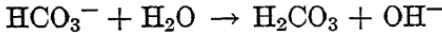


yielding the bicarbonate and the carbonate ion, respectively.

Alkali carbonates, such as Na_2CO_3 , hydrolyze to give an alkaline reaction:



Bicarbonates also undergo slight hydrolysis with the formation of H_2CO_3 :



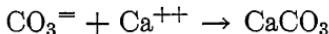
All the metallic carbonates are insoluble in water, with the exception of ammonium carbonate and the carbonates of the alkali metals. Therefore, when a sample containing soluble or insoluble salts is boiled with Na_2CO_3 (or a solid mixture is fused with Na_2CO_3), transposition will take place, precipitating the metallic ions as insoluble carbonates or, in a few instances, as basic carbonates or hydroxides. If, for example, BaSO_4 is boiled or fused with Na_2CO_3 , metathesis takes place,



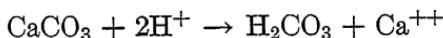
transforming the barium sulfate into barium carbonate, and leaving in solution $\text{SO}_4^=$ and Na^+ ions. This is the basis of the procedure used in systematic anion analysis, for freeing the

sample from the presence of objectional cations and, at the same time, for getting the sample into solution. The solution thus produced is referred to as the "prepared anion solution."

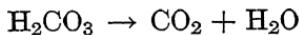
The carbonate ion is precipitated, as previously stated, by practically all cations. It is important to note that this is especially true of the cations of the group reagents, namely: Ca^{++} , Ba^{++} , Zn^{++} and Ag^+ , which form the corresponding insoluble carbonates. The reagent of this group, $\text{Ca}(\text{NO}_3)_2$, precipitates white CaCO_3 :



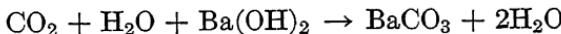
The usual test for carbonates depends upon the liberation of CO_2 by the action of an acid and the subsequent reaction of the CO_2 with $\text{Ba}(\text{OH})_2$ or $\text{Ca}(\text{OH})_2$. When a soluble or insoluble carbonate, such as CaCO_3 , is treated with an acid, even one as weakly ionized as $\text{HC}_2\text{H}_3\text{O}_2$, carbonic acid is formed:



The unstable H_2CO_3 decomposes into carbon dioxide and water:

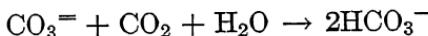


In the presence of an appreciable amount of carbonate, the evolution of CO_2 takes place with effervescence. Then, if the gas is exposed to or led into a solution of $\text{Ba}(\text{OH})_2$, insoluble BaCO_3 forms:



It should be noted that SO_2 , evolved by acidifying a sulfite or a thiosulfate, also will render $\text{Ba}(\text{OH})_2$ turbid when carbonates are tested for in the original sample. This interference is overcome, in systematic analysis, by first oxidizing the SO_2 with H_2O_2 or some other oxidizing agent, and thus making the test specific for carbonates.

Phenolphthalein Test. Carbon dioxide reacts with a carbonate to form a bicarbonate according to the equation:



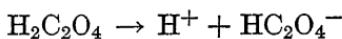
Phenolphthalein, a substance used extensively as an indicator, is pink in Na_2CO_3 solution and colorless in NaHCO_3 solution. If, therefore, a drop of this substance is rendered alkaline by Na_2CO_3 and held in the loop of a platinum wire and exposed to CO_2 , the pink color will fade. The indicator solution is prepared by mixing

2.5 ml. of a 0.5 per cent solution of phenolphthalein, 1 ml. of 0.1 *M* Na₂CO₃ and 10 ml. of water.

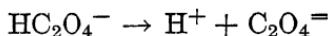
H₂SO₃, H₂S and HCN interfere with this test, since these acids also will decolorize the indicator. The interference from sulfites is overcome by the use of H₂O₂, and that from HCN and H₂S by HgCl₂.

OXALATE, C₂O₄⁼

Oxalates are the salts of oxalic acid. This organic acid is a white solid, crystallizing with 2 molecules of water, H₂C₂O₄·2H₂O. It ionizes in two stages, namely:



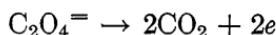
and



It yields bioxalates and normal oxalates upon reaction with bases. Most of the oxalates are relatively insoluble in water. The relative solubility of calcium, strontium and barium oxalate already has been considered in connection with the separation of calcium in group IV of the cations.

Calcium oxalate is soluble in strong acids but insoluble in dilute HC₂H₃O₂. In this respect it differs, along with CaF₂, from the calcium salts of the other members of this group; this property is used to separate calcium oxalate and calcium fluoride from the other calcium salts of this group.

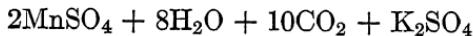
Oxalic acid and acidified solutions of oxalates are excellent reducing agents. The electron equation for the oxalate ion is:



The reduction of KMnO₄ by the oxalate ion is used as a characteristic test. If KMnO₄ is added to an acidified solution of an oxalate, the mixture will be decolorized, owing to the reduction of the pink MnO₄⁻ ion to colorless Mn⁺⁺. The reaction in ionic form is



or, in molecular form,



For the writing of this equation see page 101.

It must be remembered that many other reducing agents reduce KMnO₄ with resultant decolorization of the solution. Particularly will sulfites and arsenites, both members of this group, decolorize KMnO₄, and hence in systematic analysis special care must be exercised in the complete removal of these interfering reducing ions.

Resorcinol is sometimes used as a test for oxalates. It produces a deep blue color when applied according to the procedure outlined on page 245. Nitrates interfere with this test. This same reagent is employed as a test for tartrates (see page 246) and yields a red color when employed under somewhat different conditions than when testing for oxalates.

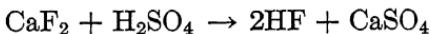
Since the oxalates of the alkaline earth group (group IV of the cations), namely, CaC₂O₄, SrC₂O₄ and BaC₂O₄, are insoluble in a neutral or alkaline solution, it is important in the systematic detection of the cations that the presence or absence of oxalates should be known before the precipitation of group III of the cations is begun; if oxalates are present, they must be removed. The method of removal consists of destroying the oxalates, along with tartrates and similar organic matter, by fuming down with concentrated H₂SO₄ and HNO₃. When oxalic acid is heated with concentrated sulfuric acid, it decomposes and yields CO, CO₂ and other products. For the manipulative details of this step in the removal of interfering oxalates, see the procedure on page 342.

FLUORIDE, F⁻

Most of the fluorides are insoluble in water, the notable exceptions being those of silver, mercury (ic), tin (ic), aluminum, sodium, potassium and ammonium.

Calcium fluoride is an important salt. It is formed when a calcium salt is added to a soluble fluoride. CaF₂, like CaC₂O₄, is insoluble in dilute acids, such as HC₂H₃O₂. The insolubility of CaF₂ in acetic acid serves to separate F⁻ as well as C₂O₄⁼ from the other members of this group.

Fluorides are derived from hydrofluoric acid, a liquid which boils at 19.4° C. The commercial acid, dispensed in non-silicate glass containers, is an aqueous solution containing about 50 per cent HF. It is a weakly ionized monoprotic acid. It is formed when a fluoride, such as CaF₂, is treated with H₂SO₄; the equation is



The most useful property of this acid is its ability to react with silica and silicates, and it therefore is employed technically for the etching of glass. Upon this property rests one of the tests for fluorides. With SiO_2 the acid forms volatile silicon tetrafluoride:



If the SiF_4 is allowed to come into contact with water this reaction takes place:

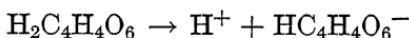


These two products are insoluble in water and render the drop turbid. This test has been modified, so that these products are taken up in ammonium molybdate, and after treatment with benzidine and sodium acetate, a blue reduction product forms.

Fluorides are tested for most easily by the zirconium-alizarin test. This is based on the facts (1) that a solution of zirconium nitrate forms a violet-colored lake with the dye, alizarin-S, and (2) that, when the fluoride ion is then added, there is formed the zirconium-hexafluoride ion, ZrF_6^- , and thus the violet lake is destroyed, and a pale yellow or colorless solution is left.

TARTRATE, $\text{C}_4\text{H}_4\text{O}_6^-$

Tartaric acid and alkali tartrates are important analytical reagents. Among the better-known salts are "Rochelle salt," $\text{NaKC}_4\text{H}_4\text{O}_6$; cream of tartar, $\text{KHC}_4\text{H}_4\text{O}_6$; and tartar emetic, $(\text{SbO})\text{KC}_4\text{H}_4\text{O}_6$. Tartaric acid is a white crystalline solid, soluble in water. As a weak diprotic acid it ionizes in two stages:



and

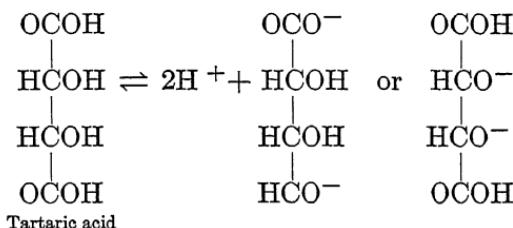


and yields the bi- or acid tartrate ion and the normal tartrate ion, respectively.

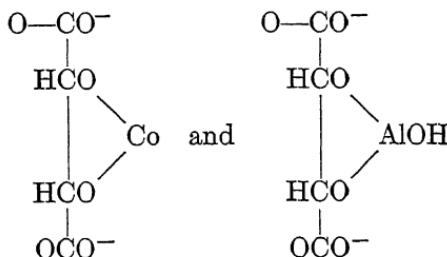
The most important property of the alkali tartrates is the readiness with which they form soluble complex ions with many metallic ions, such as Al^{+++} , Cr^{+++} , Fe^{+++} , Co^{++} , Ni^{++} , Cu^{++} , Sb^{+++} , Sn^{++++} (see page 237). For this reason, in the presence of a tartrate, many of the metallic ions fail to precipitate as hydroxides

when treated with alkalies. It is important therefore to test for tartrates and effect their removal in the systematic procedures for cation detection. Citrates, malates, sugars, starches and many other forms of organic materials behave similarly.

Tartaric acid has the structural formula shown in the following and, when ionized, yields the tartrate ion, which may have either of the two formulas:



In the cases of the complexes of cobalt and aluminum, the structures are probably



Calcium tartrate is precipitated when calcium nitrate is added to a tartrate solution.

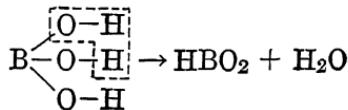
When a tartrate is heated strongly with concentrated H₂SO₄, it darkens and chars, and the decomposition products give the odor of burnt sugar. This is a common means of recognizing the presence of tartrates and similar organic substances.

If an ammoniacal solution of silver nitrate is reduced in a test tube with a tartrate solution, the silver deposits as a bright mirror on the walls of the tube. This property may be used as a test for tartrates.

Resorcinol may be used as a test reagent. This reagent, as already mentioned, also may be used as a test for oxalates. The tartrate will produce a reddish color with this reagent. Details of this test are given on page 246.

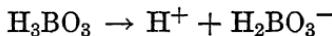
BORATE, $\text{BO}_3^=$, BO_2^- , $\text{B}_4\text{O}_7^=$

The element boron forms three acids, namely orthoboric acid, H_3BO_3 ; metaboric acid, HBO_2 ; and pyroboric acid, sometimes called tetraboric acid, $\text{H}_2\text{B}_4\text{O}_7$. In all three the valence of boron is +3. The meta and the pyro acids are derived from the ortho by the loss of water; the meta by the loss of 1 molecule of water:



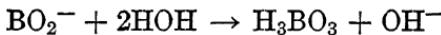
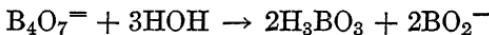
and the pyro by the loss of 5 molecules of water from 4 molecules of the orthoacid.

Orthoboric acid, sometimes also called boracic acid, is a white solid. Although it contains three replaceable hydrogens and therefore is triprotic, even its primary ionization is rather feeble, taking place in accordance with the equation:



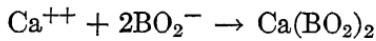
Boric acid behaves thus as a weak monoprotic acid.

The commonest salt of boron is borax, or sodium tetraborate, $\text{Na}_2\text{B}_4\text{O}_7$, derived from tetraboric acid. Borax hydrolyzes first into free boric acid and the metaborate ion, which in turn hydrolyzes still further as shown in the equations:



A solution of borax therefore contains, in addition to $\text{B}_4\text{O}_7^=$ ions, free boric acid, metaborate ions and hydroxyl ions; the solution shows an alkaline reaction. Borax, it will be recalled, is used in fused form as bead tests for cobalt and nickel. Refer to these tests under "Cobalt" and "Nickel."

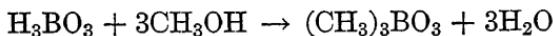
Calcium nitrate, when added to a borax solution, will precipitate the metaborate:



Barium nitrate produces a similar effect. Silver nitrate precipitates AgBO_2 from rather concentrated borax solutions; from

dilute solutions containing a greater proportion of OH^- ions, Ag_2O is precipitated.

Some of the compounds of boron are volatile and burn with a green flame. Methyl borate, $(\text{CH}_3)_3\text{BO}_3$, and ethyl borate, $(\text{C}_2\text{H}_5)_3\text{BO}_3$, are two such compounds. These compounds are produced readily by the action of the corresponding alcohols on a solution of boric acid. In the case of methyl alcohol, the equation is



This property is used in the flame test for borates.

The vegetable dye, turmeric, turns a reddish color in the presence of compounds of boron. This is the basis of the best test for boron; the procedure is described later.

SULFITE, SO_3^-

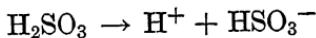
The element sulfur forms a large number of acids. The more common ones for which detection is provided in this book are hydrosulfuric (hydrogen sulfide), H_2S ; sulfurous, H_2SO_3 ; sulfuric, H_2SO_4 ; and thiosulfuric, $\text{H}_2\text{S}_2\text{O}_3$. The anion of sulfurous acid, the sulfite ion, is tested for in this group; sulfates are tested for in group II, sulfides in group III, and thiosulfates in group IV.

The free acid, sulfurous acid, H_2SO_3 , is unstable and exists only in solution. It is formed by dissolving the anhydride, SO_2 , a gas, in water:

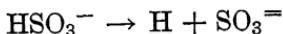


In such an aqueous solution, most of the SO_2 remains as dissolved gas, and very little is combined as H_2SO_3 . The solution is unstable.

The acid ionizes, like all diprotic acids, in two stages,



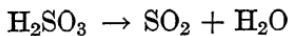
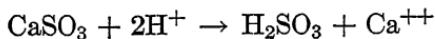
and



and gives rise to the bisulfite ion and the sulfite ion. Partial and complete neutralization of sulfurous acid by alkalies produces bisulfites and sulfites, respectively.

All sulfites, except those of the alkali metals, are practically insoluble in water. Most of the bisulfites, on the other hand, are soluble in water.

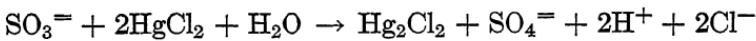
Calcium nitrate readily precipitates white CaSO_3 . The precipitate is easily soluble in acids, even dilute $\text{HC}_2\text{H}_3\text{O}_2$. Acids stronger than acetic decompose sulfites with evolution of SO_2 :



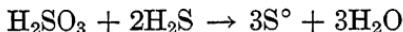
The most interesting and analytically useful property of sulfites is a strong reducing action in acid solution, the sulfite ion being oxidized to sulfate, in accordance with the electron equation:



Oxidizing agents such as $\text{K}_2\text{Cr}_2\text{O}_7$, KMnO_4 , H_2O_2 and I_2 are reduced readily. The sulfite ion likewise will reduce HgCl_2 to Hg_2Cl_2 to form a distinctive white precipitate. The reaction is used as a test for sulfites, the equation being



The oxidation of the sulfite to sulfate by means of hydrogen peroxide with the subsequent addition of BaCl_2 and precipitation of BaSO_4 is made another simple test for sulfites. But under certain other conditions, this anion also may act as an oxidizing agent. For example, toward H_2S it acts as an oxidant, in an acid solution:



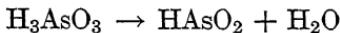
Sodium nitroprusside, $\text{Na}_2[\text{Fe}(\text{CN})_5]\text{NO}$, when added to a few drops of a sulfite solution which has been treated with ZnSO_4 and $\text{K}_4\text{Fe}(\text{CN})_6$, according to the procedure given later, yields a red color and is a distinctive test for sulfites.

ARSENITE, $\text{AsO}_2^- (\text{AsO}_3^{=})$

Arsenic is a rather strongly acidic element and in its compounds exists mainly in the anion form, with a valence of either +3 or +5. The most important compounds in which arsenic is present as cation are As_2S_3 and As_2S_5 . The anion forms are the several arsenite ions and the corresponding arsenate ions.

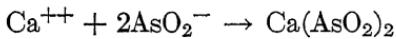
Arsenites, in their relation to the detection of arsenic among the cations, already have been discussed in division B of group II of the cations, to which the student should now refer (see page 223)

The most important of the trivalent compounds of arsenic are meta-arsenious acid, HAsO_2 , and the sulfide, As_2S_3 . The acid is derived from As_2O_3 , which when dissolved in water first forms the ortho acid, which then passes over into the meta form:



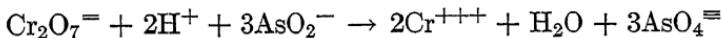
The oxide is soluble in acids and in bases, being therefore an amphoteric substance. The acid exists only in solution. The test solution, NaAsO_2 , is derived from the meta acid.

Many arsenites are insoluble in water. Thus, calcium meta-arsenite is readily precipitated by calcium ion as $\text{Ca}(\text{AsO}_2)_2$:



This precipitate dissolves in acetic acid as well as in stronger acids.

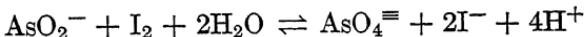
The arsenite ion is a strong reducing agent and is easily oxidized by oxidizing agents, especially in an acid solution. Thus, if a mixture of arsenite and chromate, such as one might have in a sample, is acidified, rapid reduction of the dichromate to chromic ion takes place.



This reduction takes place to a slight extent, even in an alkaline solution, but not sufficiently to make the detection of arsenite impossible.

Potassium permanganate is reduced and decolorized by the arsenite ion in an acid solution, and, for this reason, when KMnO_4 is used as the test reagent for oxalates, arsenites as well as sulfites must be thoroughly washed out of the CaC_2O_4 residue.

The oxidizing agent used to detect arsenites is iodine; the reaction is



Special attention is called to this reversible reaction, since the test for arsenates, as described later, consists of reducing the arsenate ion with the iodide ion. This is the reverse of the preceding reaction.

Hydrogen sulfide produces an immediate rapid precipitation of yellow arsenious sulfide, As_2S_3 . Silver nitrate will give a yellow

precipitate of AgAsO_2 . Ammonium molybdate and magnesia mixture, important reagents for the detection of arsenates, do not react with the arsenite ion, and this property distinguishes arsenites from arsenates.

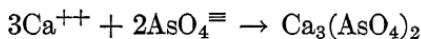
ARSENATE, $\text{AsO}_4^{=}$

Arsenates are derived from arsenic acid; this, in turn, is derived from As_2O_5 :



Arsenic acid as a triprotic acid undergoes ionization in three stages, producing the primary, secondary and tertiary arsenate ions, H_2AsO_4^- , $\text{HAsO}_4^{=}$ and $\text{AsO}_4^{=}$, respectively. Arsenates are analogous to the corresponding orthophosphates. The anion test solution is made from disodium arsenate, Na_2HAsO_4 .

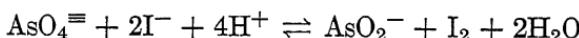
Calcium nitrate precipitates the normal or tertiary arsenate,



readily soluble in dilute $\text{HC}_2\text{H}_3\text{O}_2$.

Tests for arsenic, as already described on page 223, consist in the precipitation of (1) ammonium arsenomolybdate, $(\text{NH}_4)_3\text{AsO}_4 \cdot 12\text{MoO}_3$; (2) magnesium ammonium arsenate, $\text{MgNH}_4\text{AsO}_4$, and (3) Ag_3AsO_4 . In the presence of phosphates, these tests for $\text{AsO}_4^{=}$ cannot be performed, since the $\text{PO}_4^{=}$ ion produces similar results with the reagents employed. The Gutzeit test is not employed as a specific test for arsenates, because any form of arsenic will give this test.

The test recommended here consists of the reduction of the arsenate ion with potassium iodide in a strongly acid solution:



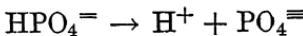
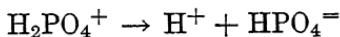
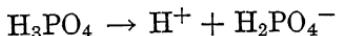
This is the reverse of the test for the arsenite ion in which the latter is oxidized by iodine.

PHOSPHATE, $\text{PO}_4^{=}$

The element phosphorus exhibits two valence states, namely, +3 and +5, in keeping with the other elements of its family, bismuth, antimony, arsenic and nitrogen. There are therefore two series of acids, analogous to those of arsenic. In the pentavalent

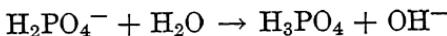
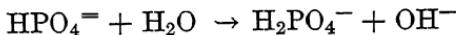
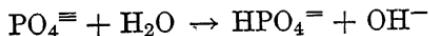
state phosphorus forms three well-known phosphoric acids: orthophosphoric acid, H_3PO_4 ; metaphosphoric acid, HPO_3 ; and pyrophosphoric acid, $\text{H}_4\text{P}_2\text{O}_7$. In the trivalent state it forms phosphorus acid, H_3PO_3 . Only the orthophosphoric acid will be considered here.

Orthophosphoric acid, in the pure state, is a white solid. Ordinarily, it is a thick syrupy solution containing about 85 per cent of H_3PO_4 . It ionizes in three stages:

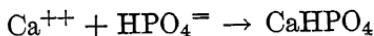


the extent of the ionization of a 0.1 M solution being, respectively, about 27, 0.1 and 0.0001 per cent. There exist therefore three series of salts, derived by the successive neutralization of the 3 replaceable hydrogens from orthophosphoric acid, and known as primary, secondary and tertiary orthophosphates, as, for example, NaH_2PO_4 , Na_2HPO_4 and Na_3PO_4 .

Phosphate ions, when in solution, undergo partial hydrolysis according to the equations:



The test solution used in the laboratory is prepared from the disodium salt, Na_2HPO_4 . Most of the phosphates are insoluble in water; practically all are soluble in acids. From a practically neutral solution of Na_2HPO_4 , calcium nitrate will precipitate CaHPO_4 :



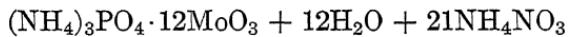
In a strongly alkaline solution, such as exists during the group precipitation, the addition of $\text{Ca}(\text{NO}_3)_2$ produces mainly the normal or tertiary phosphate, $\text{Ca}_3(\text{PO}_4)_2$. This compound is soluble in dilute acetic acid. Barium, zinc and silver ions form similar insoluble phosphates.

Like the arsenate ion, the phosphate ion will react with ammonium molybdate in a nitric acid solution to form a finely crystall-

line yellow precipitate of ammonium phosphomolybdate. The ionic equation is

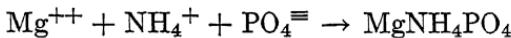


In molecular form this equation becomes



In the systematic detection of phosphates in samples which also contain arsenates, this reaction can be utilized only as a test for phosphates, *after* the removal of the arsenic. In the scheme outlined later, arsenates, as well as arsenites, are precipitated and removed by treatment with H_2S .

With magnesia mixture, the PO_4^{\equiv} ion, like the AsO_4^{\equiv} ion, forms a white crystalline precipitate of magnesium ammonium phosphate:



This reaction, it will be recalled (see "Magnesium," page 79), is an important one for the separation, detection and determination of magnesium.

PRELIMINARY EXPERIMENTS

1. Action of Group Reagent. In 9 separate centrifuge tubes labelled, respectively, CO_3^{\equiv} , $\text{C}_2\text{O}_4^{\equiv}$, F^- , SO_3^{\equiv} , BO_2^- , AsO_2^- , AsO_4^{\equiv} , PO_4^{\equiv} and $\text{C}_4\text{H}_4\text{O}_6^{\equiv}$ place 5 drops of the designated anion test solution (these test solutions contain 2 milligrams of the anion per milliliter). Add a drop of saturated $\text{Ca}(\text{OH})_2$, (limewater), to each tube. Then add, dropwise, the group reagent, 1 M $\text{Ca}(\text{NO}_3)_2$ until precipitation appears complete. Observe the physical nature of each precipitate. Note that all are white. Record these observations and write the equations. Reserve the contents of the tubes for later experiments.

2. Action of Acetic Acid on Group Precipitates. Centrifuge the tubes from experiment 1, in pairs, and discard the centrifugates. To each, add dilute (12.5 per cent) $\text{HC}_2\text{H}_3\text{O}_2$ until the solution is distinctly acid. Which of the calcium salts remain as precipitates? Write the reactions for those precipitates which dissolve. Was effervescence observed in any instance?

3. Test for Carbonate. (a). Precipitate some CaCO_3 by adding a few drops of the group reagent to 5 drops of test solution, shake, and centrifuge. Have in readiness a drop of $\text{Ba}(\text{OH})_2$ suspended in the loop of a platinum wire. Then add a drop or two of dilute HCl or $\text{HC}_2\text{H}_3\text{O}_2$ to the CaCO_3 , holding the drop of test reagent over the mouth of the tube. Observe whether the drop of

$\text{Ba}(\text{OH})_2$ becomes turbid. What is formed? Note whether the turbidity clears up. Write the equations. What other gas could cause a turbidity in $\text{Ba}(\text{OH})_2$ solution?

(b) Add to a mixture of $\text{CO}_3^{=}$ and $\text{SO}_3^{=}$ test solutions 2 drops of H_2O_2 , and then acidify with dilute HCl. What is the gas which escapes? Write the equation by which the SO_2 was prevented from forming.

4. Tests for Oxalate and Fluoride. (a). Transfer the precipitates of CaC_2O_4 and CaF_2 , which were obtained in experiment 1 and which remained insoluble in the $\text{HC}_2\text{H}_3\text{O}_2$ in experiment 2, to another tube, mixing the precipitates thoroughly. Remove a portion of the mixed precipitate to a test tube, add a drop or two of dilute sulfuric acid to dissolve the CaC_2O_4 , heat, and then add a small drop of very dilute KMnO_4 reagent. What happens? Is the solution decolorized? Give the equation for this *redox* reaction.

To a few drops of oxalate test solution, add a few specks of magnesium powder, warm, and then add 5 drops of resorcinol reagent. Note the colored ring that forms.

(b) To show the presence of fluoride, add to the remainder of the mixed precipitate more dilute H_2SO_4 , and then gradually dilute KMnO_4 until an excess has been added and the solution remains pink. This is done to destroy the oxalate, which would interfere with the fluoride test. Then destroy the excess of KMnO_4 with H_2O_2 solution. On a spot plate mix a drop of zirconium nitrate reagent with a drop of alizarin-S dye solution; the mixture should be red. Now add a drop of the solution freed from oxalate. Explain why the red color is discharged.

5. Tests for Borate. (a). Heat some water to boiling in a beaker. Cover with a watch glass. Place a drop of borate test solution, acidified with HCl, on a strip of tumeric test paper, and place it on the watch glass. Examine it when dry; it should have a reddish or pink color. Repeat the dipping and drying if the color does not show up. Treat the spot with a tiny drop of *very* dilute NaOH. What color is the spot now?

(b) Place 10 drops of borate test solution in a crucible, and add 5 drops of concentrated H_2SO_4 and 5 drops of methyl or ethyl alcohol. Warm, and ignite the vapors. Observe the color of the flame. Write the equations for the reactions between boric acid and ethyl or methyl alcohol.

6. Tests for Sulfite. (a). Add a few drops of H_2O_2 to a few drops of test solution. To what is the sulfite oxidized? Write the equation. Then add a drop of BaCl_2 reagent and a drop of dilute HCl. What is the white precipitate which forms? Give the equation for the reaction.

(b) Add to a few drops of boiling hot saturated HgCl_2 solution 2 drops of test solution. What forms? Note the changing color of the precipitate. Write the equations.

(c) On a spot plate mix a drop each of $\text{K}_4\text{Fe}(\text{CN})_6$, saturated ZnSO_4 and sodium nitroprusside. Then add a drop of test solution. Observe, and record what happens.

7. Tests for Arsenite, Arsenate and Phosphate. To a centrifuge tube add 5 drops each of arsenite, arsenate and phosphate test solution. Mix well.

(a) Withdraw 2 drops of the solution, and dilute it with 3 drops of water. To a drop of starch indicator solution, add 2 drops of dilute iodine solution; note the blue color of the adsorbed iodine in the starch. Then add a drop of

this solution to the diluted mixture. Observe what happens. This is the test for arsenite. Write the equation.

(b) Withdraw 2 more drops of the original mixture, and add a drop of concentrated HCl and a small crystal of potassium iodide. Does the mixture change color? Add a drop of starch indicator; to what is the blue color due? This is the test for arsenate. Write the equation; compare this reaction with the one for arsenites.

(c) Because the reagent for the phosphate test, ammonium molybdate, yields a yellow precipitate with arsenates as well as with phosphates, the arsenate ion must be removed before the test for the phosphate ion is carried out. To the remainder of the mixture in the centrifuge tube, add a crystal of Na_2SO_3 and a drop of concentrated HCl, heat to boiling in the water bath, and then pass in H_2S . Centrifuge the yellow precipitate. Write the equation for the reduction of arsenate by sulfite ion. Boil the centrifugate to remove H_2S , testing with lead acetate test paper.

To part of the solution, add a drop of concentrated HNO_3 , a small crystal of NH_4NO_3 and a few drops of $(\text{NH}_4)_2\text{MoO}_4$ reagent; heat nearly to boiling. Give the formula of the yellow precipitate which forms.

8. Tests for Tartrate. (a). Mix several drops of tartrate test solution with an equal volume of concentrated H_2SO_4 in a crucible, and heat strongly over a flame. Cautiously smell the vapors, as charring takes place.

(b) Place several drops of tartrate test solution in a test tube, add a few specks of magnesium powder, and then add 5 drops of the resorcinol reagent. What color is produced? Compare the color here with that produced with oxalates.

REVIEW EXERCISES

1. Write ionic equations showing the formation of the calcium salts of this group. What ions of this group are reducing in their nature? Name the oxidizing ion of this group. What means is taken to prevent the interaction of oxidizing and reducing ions in this systematic scheme?

2. Complete and balance, using electron equations, the equations representing the action of

- (a) KMnO_4 on $\text{H}_2\text{C}_2\text{O}_4$ in H_2SO_4 solution
- (b) HgCl_2 on H_2SO_3
- (c) I_2 on AsO_2^-
- (d) I^- on AsO_4^{3-}

3. Explain, from an equilibrium standpoint, why CO_2 is evolved when CaCO_3 is treated with dilute $\text{HC}_2\text{H}_3\text{O}_2$. Explain, likewise, why $\text{HC}_2\text{H}_3\text{O}_2$ will not dissolve CaC_2O_4 .

4. Show by an equation how Na_2SO_3 acts to reduce the arsenate ion to the arsenite form. Why is this desirable in systematic analysis? How are arsenates, and arsenites as well, removed in order for a test for phosphate ion to be applied?

5. Write the equation for the phosphate test, using ammonium molybdate in a nitric acid solution. Show, by writing the corresponding equation for

H_3AsO_4 , why arsenates must be removed before the molybdate test is decisive for phosphates.

6. An unknown sample is divided into two portions, one to be analyzed for the cations, and the other for the anions. If arsenite or arsenate is found in the anion analysis, would you expect to find arsenic in the cation analysis? Explain.

7. Combine the equation for the arsenite test with that for the arsenate test into a reversible reaction. Explain how it is possible to use this reversible reaction as tests for both anions.

8. Complete and balance the equations for the oxidation of

- (a) $\text{SO}_3^{=}$ by MnO_4^{-} in an acid solution
- (b) $\text{SO}_3^{=}$ by $\text{Cr}_2\text{O}_7^{=}$ in an acid solution
- (c) AsO_2^{-} by MnO_4^{-} in an acid solution
- (d) AsO_2^{-} by $\text{Cr}_2\text{O}_7^{=}$ in an acid solution

9. From the solubility of CaC_2O_4 calculate the $K_{s.p.}$ of this compound.

10. What volume of calcium nitrate solution ($1 M$) must be added to precipitate quantitatively the $\text{C}_2\text{O}_4^{=}$ and F^{-} from a mixture made by mixing 1 ml. each of test solutions containing 10 milligrams of the ion?

OUTLINE OF METHOD OF ANALYSIS OF THIS GROUP

The group is precipitated as a whole by $\text{Ca}(\text{NO}_3)_2$. The calcium salts are all white; hence, no distinguishing color can be used to indicate the presence of any individual anion. The solution is kept alkaline with $\text{Ca}(\text{OH})_2$ in order to lessen, as far as possible, the interaction of oxidizing and reducing ions.

By the use of dilute acetic acid, (a) the calcium carbonate is decomposed with liberation of CO_2 , (b) CaC_2O_4 and CaF_2 remain insoluble, and (c) all other calcium salts are dissolved.

In the solution resulting from the action of acetic acid, tests can be made directly for borate, sulfite, arsenite, arsenate and tartrate, by methods already described and carried out under preliminary experiments.

In order for the phosphate ion to be identified, the arsenate ion must be removed. This is accomplished by first reducing the latter to the arsenite form and then precipitating and separating it as As_2S_3 .

Mention should be made of the possible presence of silicates in samples of unknown composition. If silicate is present in soluble form, a part of it at least will be precipitated as calcium silicate and remain in the residue insoluble in acetic acid. A special method, however, is described on page 347 for the detection of silicates.

TABLE XIX
DIAGRAMMATIC OUTLINE OF ANALYSIS OF GROUP I

Solution	Precipitate	
CO_3^-	<u>CaCO_3</u>	CO_2^- —test on orig. sample + $\text{Ba}(\text{OH})_2$ \rightarrow turbid drop
C_2O_4^-	<u>CaC_2O_4</u>	<i>Residue</i>
F^-	Add <u>CaF_2</u>	CaC_2O_4 } $\text{H}_2\text{SO}_4 \rightarrow$ decolorizes CaF_2 } $\text{KMnO}_4 + \text{alizarine} +$ Add $\text{Zr}^{++} \rightarrow [\text{ZrF}_6]^{m}$ yellow
BO_2^-	<u>$\text{Ca}(\text{BO}_2)_2$</u>	<i>Solution</i>
SO_3^-	<u>CaSO_3</u>	$\text{BO}_2^- + \text{turmeric} \rightarrow$ pink
$\text{C}_4\text{H}_4\text{O}_6^-$	<u>$\text{CaC}_4\text{H}_4\text{O}_6$</u>	$\text{SO}_3^- + \text{nitroprusside} \rightarrow$ red
AsO_2^-	<u>$\text{Ca}(\text{AsO}_2)_2$</u>	$\text{C}_4\text{H}_4\text{O}_6^- + \text{H}_2\text{SO}_4 \rightarrow$ chars
$\text{AsO}_4^{=}$	<u>$\text{Ca}_3(\text{AsO}_4)_2$</u>	$\text{AsO}_2^- + \text{I}_2$ (starch) \rightarrow decolorizes
$\text{PO}_4^{=}$	<u>$\text{Ca}_3(\text{PO}_4)_2$</u>	$\text{AsO}_4^{=} + \text{KI} + \text{HCl}$ (starch) $\rightarrow \text{I}_2$ blue, remove AsO_4^- and AsO_2^- with H_2S $\text{PO}_4^{=} + (\text{NH}_4)_2\text{MoO}_4 \rightarrow (\text{NH}_4)_3\text{PO}_4 \cdot$ <u>12MoO_3</u> yellow

PROCEDURE OF ANALYSIS OF GROUP I

The sample submitted will contain only members of group I, and it will have been made alkaline with $\text{Ca}(\text{OH})_2$.

Detection of Carbonates. Make a loop in the platinum wire, and suspend in the loop a drop of $\text{Ba}(\text{OH})_2$ reagent. To about 10 drops of the sample in a test tube, add 5 drops of H_2O_2 to oxidize sulfites if present, and then acidify with dilute HCl, holding the test drop of $\text{Ba}(\text{OH})_2$ over the mouth of the tube. A fairly vigorous effervescence, together with the formation of a turbidity or cloudiness in the suspended test drop, shows the presence of carbonates in the sample.

Group Precipitation. Place 1 ml. of the sample in a centrifuge tube, and add, dropwise, enough $\text{Ca}(\text{NO}_3)_2$ reagent to insure complete precipitation. Centrifuge, and wash the precipitate several times with very dilute calcium nitrate reagent. Test the final washings for nitrates with ferrous sulfate and H_2SO_4 as described on page 302. The precipitate may contain CaCO_3 , CaC_2O_4 , CaF_2 , $\text{Ca}(\text{BO}_2)_2$, CaSO_3 , $\text{Ca}(\text{AsO}_2)_2$, $\text{Ca}_3(\text{AsO}_4)_2$, $\text{Ca}_3(\text{PO}_4)_2$ and $\text{CaC}_4\text{H}_4\text{O}_6$.

To the well-washed precipitate, add 10 drops of dilute ($3 M$, 12.5 per cent) $\text{HC}_2\text{H}_3\text{O}_2$, stir thoroughly, and centrifuge. The treatment with acetic acid will decompose the carbonate and CO_2 will evolve. The residue may be $\text{Ca}_2\text{C}_2\text{O}_4$ or CaF_2 or both. If tartrate is present in large quantity, some of the $\text{CaC}_4\text{H}_4\text{O}_6$ may

remain undissolved. In the centrifugate may be BO_2^- , SO_3^- , AsO_2^- , $\text{AsO}_4^{=}$, $\text{PO}_4^{=}$ and $\text{C}_4\text{H}_4\text{O}_6^-$ ions.

Detection of Oxalate. Treat the residue with another 5 drops of $\text{HC}_2\text{H}_3\text{O}_2$, centrifuge, and wash repeatedly, until a drop of the last washings no longer decolorizes a tiny drop of dilute iodine solution, containing starch indicator; that is, continue washing until a blue color remains in the iodine solution. This step is imperative in order to remove the last traces of the other reducing ions, sulfite or arsenite, which may be present.

Treat the thoroughly washed residue with dilute H_2SO_4 . Remove several drops, heat, and add a tiny drop of dilute KMnO_4 reagent. If oxalates are present, the test mixture will be decolorized, owing to the reduction of the pink MnO_4^- ion by the oxalate ion.

Detection of Fluoride. If oxalates have been found, continue to add the dilute KMnO_4 until the solution becomes purple or brown. This is done to destroy the oxalate. Then add 1 or 2 drops of 3 per cent H_2O_2 , until the color is discharged; this removes the excess of KMnO_4 . On a spot plate, prepare the zirconium-alizarin lake by mixing 1 drop of zirconium nitrate with 2 drops of alizarin S solution. Finally, add a drop of the solution to be tested for fluorides. If fluorides are present, the red color will change to a light yellow or straw color.

Detection of Tartrate. To a 2-drop portion of the solution in a crucible, add a drop of concentrated H_2SO_4 , and heat the crucible. The heavy black or brown char shows the presence of tartrate in the sample.

Detection of Borate. Heat a beaker of water to boiling. Take a portion of the acetic acid solution obtained in dissolving the group precipitate, dip into it a strip of tumeric test paper, acidify with a drop of dilute HCl, place the paper on a watch glass, and place this, in turn, over the beaker of boiling water in order to dry it. If borate is present, the paper will turn pink. Touch a drop of very dilute NaOH to the pink stain, which then should turn green if borates are present.

Identification of Sulfite. On the spot plate place a few drops of a saturated solution of ZnSO_4 and a drop of freshly prepared potassium ferrocyanide, $\text{K}_4\text{Fe}(\text{CN})_6$, together with 1 or 2 drops of sodium nitroprusside. Then add a drop of the solution to be tested for sulfites. If a red color develops in the mixture, a sulfite is shown to be present.

To test for arsenites and arsenates, sulfites must be absent; therefore, if the test for sulfites was positive, boil a portion of the acetic acid solution, until sulfites are completely removed, as may be proved by repeating the sulfite test on the boiled solution.

Detection of Arsenite. To a drop of the boiled acetic acid solution, free from sulfite, add 5 drops of water and a drop of dilute iodine solution to which starch has been added. If the blue color is discharged, arsenites are proved to be present.

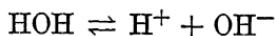
Detection of Arsenate. To another drop of the boiled solution, add a drop of concentrated HCl and a fragment of potassium iodide. If the solution turns brown, owing to liberation of free I₂, arsenates are shown to be present. In case doubt exists, add a drop of dilute starch solution, in which case a blue color will develop if arsenates are present.

Detection of Phosphate. If arsenates or arsenites are shown to be present, they must be removed before the test for phosphates is made. In this case proceed as follows: Treat about 10 drops of the remaining solution with a few crystals of Na₂SO₃ to reduce the arsenate, make strongly acid with a drop of concentrated HCl, heat, and pass in H₂S until the precipitation of arsenious sulfide is complete. Centrifuge, and boil the supernatant solution until the odor of H₂S can no longer be detected.

Now, to a few drops of this solution, add a drop of concentrated HNO₃, warm, and then add 5 drops of ammonium molybdate. A yellow precipitate of (NH₄)₃PO₄ · 12MoO₃, which may be slow in forming, shows the presence of phosphates. If the solution becomes blue, it indicates reduction of the molybdate reagent due to incomplete removal of H₂S. In this case repeat the procedure.

THE pH VALUE OF SOLUTIONS

The Water Equilibrium. Water in its behavior as a weak electrolyte ionizes to a very small extent into hydrogen ions and hydroxyl ions according to the equation:



By application of the Law of Chemical Equilibrium to this reaction the equilibrium expression becomes

$$\frac{C_{\text{H}^+} \times C_{\text{OH}^-}}{C_{\text{HOH}}} = K_{\text{ion of H}_2\text{O}}$$

The constant in this equation is the true ionization constant of water, and its value is approximately 1×10^{-16} at 25° C. We may judge, from the small value of this constant, that the concentrations of H⁺ ion and OH⁻ ion present in water are extremely small and that the mass of non-ionized water in equilibrium with its ions is enormous and, moreover, may be considered practically constant.

We may then write the equilibrium expression in the form,

$$C_{\text{H}^+} \times C_{\text{OH}^-} = K_{\text{ion}} \times C_{\text{HOH}}$$

by transferring the factor C_{HOH} . A liter of water at 25° C. weighs 997 grams; 997 ÷ 18 (the molecular weight of water) equals 55.4; a liter of water consists of 55.4 gram moles; we may say that the concentration of water in a liter of water is 55.4 M. The product of the concentrations of the ions in a liter of pure water is therefore of the order of 10^{-14} . More accurate determinations of the concentrations of H⁺ and OH⁻ at 25° C. have established the value 1.2×10^{-14} as the product of H⁺ and OH⁻ in a liter of pure water. The equation,

$$C_{\text{H}^+} \times C_{\text{OH}^-} = K_w = 1.2 \times 10^{-14}$$

is known as the water equilibrium, and the constant, K_w , the water constant. Note that K_w is a modified or derived ionization constant, in the same sense that the expression $(C_{\text{H}^+})^2 \times C_{\text{S}^-} = 1.1 \times 10^{-23}$ defines the concentrations of H⁺ and S⁻ in equilibrium with H₂S.

The value of 1.2×10^{-14} may be transformed into a pure exponent. K_w expressed as a pure exponent is then $1 \times 10^{-13.92}$.

The fact that the ionization of water produces H⁺ ions and OH⁻ ions in equal amounts leads to the important conclusion that the concentrations of both H⁺ ion and OH⁻ ion in a liter of pure water at 25° C. are approximately 1×10^{-7} . Three much more significant deductions, moreover, follow from the relationship:

$$C_{\text{H}^+} \times C_{\text{OH}^-} = 1.2 \times 10^{-14}$$

They are:

1. All aqueous solutions contain both hydrogen and hydroxyl ions.
2. In all aqueous solutions the product of the H⁺ ion and OH⁻ ion concentrations must equal 1.2×10^{-14} at 25° C.
3. Hydrogen and hydroxyl ions derived from the water as the solvent may alter the concentrations of other ions present in aqueous solutions.

Neutrality, Acidity and Basicity of Solutions. A neutral solution is defined as one that contains equal concentrations of H^+ ion and OH^- ion, that is, an excess of neither ion. By virtue of the K_w relationship, a neutral solution must contain 10^{-7} gram ion of H^+ and 10^{-7} gram ion of OH^- per liter of solution. Pure water, unaffected by dissolved material, is theoretically neutral and contains 10^{-7} gram ion of H^+ ion and the same concentration of OH^- ion per liter (at the reference temperature, 25° C.).

An acidic solution contains an excess of H^+ ions over OH^- ions, and, since neutrality is reached at a concentration of 10^{-7} for H^+ ions, any aqueous solution whatsoever which contains a hydrogen-ion concentration greater than 10^{-7} is an acidic solution. If, for example, a certain solution has a hydrogen-ion concentration of 10^{-4} , the solution is acidic; the hydroxyl-ion concentration in this same solution must be approximately 10^{-10} , since the relationship $C_{H^+} \times C_{OH^-} = 10^{-14}$ must be satisfied.

A basic solution is one that contains an excess of OH^- ions over H^+ ions. A solution to be basic must contain a concentration of OH^- ions greater than 10^{-7} . A solution containing, for example, a hydroxyl-ion concentration of 10^{-3} is basic and must have in equilibrium a hydrogen-ion concentration of 10^{-11} .

The greater concentration of H^+ ions over that of OH^- ions in an acidic solution may be due to (1) the presence of an ionizable acid, (2) the presence of an acid salt, (3) the repression of hydroxyl ions on account of the displacement of the water equilibrium by the hydrolysis of a salt, with the consequent increase of hydrogen ions. Since the H^+ ion concentration is a measure of the acidity of a solution, we can, in solutions formed by dissolving acids in water, calculate in a simple manner the acidity of the resulting solution, provided we know the molarity and the degree of ionization. Thus, a 0.1 M solution of a strong monoprotic acid such as HCl (assumed here to be completely ionized) has a H^+ ion concentration of 10^{-1} . On the other hand, a 0.1 M solution of the weakly ionized acetic acid, if it is assumed that the ionization is 1 per cent, will have a H^+ ion concentration of 10^{-3} . The hydrogen-ion concentration in the first case is 100 times that of the second case.

In the cases of the ionization of acid salts, as, for example, $NaHSO_4$, the first step in the ionization is



The bisulfate ion further ionizes,



to yield a definite, though small, concentration of hydrogen ions which renders the solution acidic.

Acidity due to hydrolysis is considered in a later section.

Conversely, the higher concentration of OH^- ions over that of H^+ ions in basic solutions may be due to (1) the presence of an ionizable hydroxide, (2) the presence of a basic salt, (3) the repression of the hydrogen-ion concentration on account of hydrolysis.

Characterization of Aqueous Solutions. In view of the interdependence of the H^+ ion and OH^- ion concentrations in all aqueous solutions, since the water equilibrium constant must be satisfied, it is apparent that, if either C_{H^+} or C_{OH^-} is known or can be found, its evaluation is sufficient to characterize the nature of the solution as acidic, neutral or basic. Since $C_{\text{H}^+} \times C_{\text{OH}^-} = 10^{-14}$, all solutions containing a C_{H^+} down to 10^{-7} are acidic, one of 10^{-7} is neutral, and all with C_{H^+} values of less than 10^{-7} are basic. This is shown in Table XX.

TABLE XX
VARIATION OF pH FOR SOLUTIONS OF HCl AND NaOH

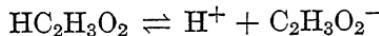
	Molarity	C_{H^+}	pH	C_{OH^-}
acidic	1.0	10^0	0	10^{-14}
	0.1	10^{-1}	1	10^{-13}
	0.01	10^{-2}	2	10^{-12}
	0.001	10^{-3}	3	10^{-11}
	0.0001	10^{-4}	4	10^{-10}
	0.00001	10^{-5}	5	10^{-9}
	0.000001	10^{-6}	6	10^{-8}
	water; or neutrality	10^{-7}	7	10^{-7}
	0.000001	10^{-8}	8	10^{-6}
	0.00001	10^{-9}	9	10^{-5}
basic	0.0001	10^{-10}	10	10^{-4}
	0.001	10^{-11}	11	10^{-3}
	0.01	10^{-12}	12	10^{-2}
	0.1	10^{-13}	13	10^{-1}
	1.0	10^{-14}	14	10^0

The Evaluation of Hydrogen-Ion Concentrations. The C_{H^+} value of a solution may be either calculated from the proper data or experimentally determined. The calculation of gram-ion concentrations from ionization data and from ionization con-

stants already has been considered. To offer an example in review, let us take the case of a 0.1 *M* solution of $\text{HC}_2\text{H}_3\text{O}_2$.

Example 1. Calculate the hydrogen-ion concentration in a 0.1 *M* solution of $\text{HC}_2\text{H}_3\text{O}_2$.

A 0.1 *M* solution of $\text{HC}_2\text{H}_3\text{O}_2$ is 1.34 per cent ionized, the ionization taking place in accordance with the reaction:



Since 0.0134 of 0.1 gram mole is ionized into H^+ ions (and $\text{C}_2\text{H}_3\text{O}_2^-$ ions), the H^+ ion concentration is

$$\begin{aligned} 0.1 \times 0.0134 &= 0.00134 \\ &= 1.34 \times 10^{-3} \end{aligned}$$

It is sometimes desirable to have this value expressed as a pure exponent. To do this, the logarithm of 1.34 is added algebraically to -3 . The logarithm of 1.34 is 0.127.

$$\begin{aligned} 1.34 \times 10^{-3} &= 1 \times 10^{-3} \times 1 \times 10^{0.127} \\ &= 1 \times 10^{-2.87} \end{aligned}$$

The OH^- ion concentration of the solution in this example can as well be readily found by subtracting the hydrogen-ion concentration, expressed in the pure exponential form, from 10^{-14} , or more accurately from $10^{-13.92}$.

Example 2. What is the OH^- ion concentration of a 0.1 *M* solution of $\text{HC}_2\text{H}_3\text{O}_2$?

$$C_{\text{H}^+} \times C_{\text{OH}^-} = K_w$$

$$C_{\text{OH}^-} = \frac{K_w}{C_{\text{H}^+}} = \frac{1 \times 10^{-13.92}}{1 \times 10^{-2.87}}$$

$$\begin{aligned} C_{\text{OH}^-} &= 1 \times 10^{[-13.92 - (-2.87)]} \\ &= 1 \times 10^{-11.05} \end{aligned}$$

Hydrogen-ion concentrations may be calculated, as shown on page 162, by means of the Ostwald dilution formula. As given on page 160, the formula is

$$M \left(\frac{\alpha^2}{1 - \alpha} \right) = K_{\text{ion}}$$

or, in approximate form,

$$M\alpha^2 = K_{\text{ion}}$$

where M is the molarity of the solution and α is the degree of ionization. From the calculated value of α the actual H^+ ion concentration can be found by multiplying α by the molarity of the solution.

By use of hydrolysis constants, as explained in the next chapter, the hydrogen- (or hydroxyl-) ion concentration in solutions which have undergone hydrolysis can be calculated.

The Experimental Determination of Hydrogen-Ion Concentration. There are two experimental methods for the measurement of the hydrogen-ion concentration of solutions—the colorimetric and the potentiometric. The colorimetric method depends upon the fact that certain organic dyestuffs have the property of changing their color over definite narrow ranges of H^+ ion concentration. (These are the substances used as indicators in neutralization titrations in volumetric quantitative analysis.) If, then, we wish to determine the (approximate) H^+ ion concentration of a solution, we may add drops of the dyestuffs to portions of the sample and in this way find the range between which two indicators are sensitive. For example, methyl orange has a yellow color in solutions which have a H^+ ion concentration of $1 \times 10^{-4.4}$ or less, and Congo red has a blue-violet color in solutions of a H^+ ion concentration greater than $1 \times 10^{-5.2}$. Consequently, if the sample is yellow in methyl orange and blue-violet in Congo red, the H^+ ion concentration lies between $1 \times 10^{-4.4}$ and $1 \times 10^{-5.2}$.

The Potentiometric Determination of Hydrogen-Ion Concentration. This method depends upon measuring the electromotive force produced in an electrolytic cell; one "half-cell" consists of a hydrogen electrode which dips into a solution which is molar with respect to H^+ ions; the other "half-cell" is made up of a hydrogen electrode dipping into the solution, the hydrogen-ion concentration of which is to be determined. The two half-cells are joined by a U-tube filled with a conducting liquid, and the electrodes are joined to a potentiometer. The voltage read on the potentiometer is related to the concentrations in the two half-cells by the following modification of the Nernst equation:

$$E = 0.059 \log \frac{1}{C_{H^+}}$$

in which 0.059 is a constant, 1 is the H^+ ion concentration in the molar solution and C_{H^+} is the H^+ ion concentration in the unknown sample. By measuring E , the equation can be solved for C_{H^+} .

***pH* Values.** In order to obviate a logarithmic calculation, a convention, first proposed by Sorenson, has been adopted, namely, to let the symbol *pH* stand for $\log 1/C_{\text{H}^+}$. According to this, the *pH* value is the logarithm of the reciprocal of the H^+ ion concentration. If, in a potentiometric determination, the voltage is measured, the *pH* becomes directly

$$\frac{E}{0.059} = \log \frac{1}{C_{\text{H}^+}} = \text{pH}$$

The use of the *pH* scale is illustrated in the following examples.

(In a similar manner the designation *pOH* may be used to designate the hydroxyl-ion concentration.)

Example 3. What is the *pH* value of a solution, the C_{H^+} of which is known to be 1×10^{-5} ?

Since

$$\begin{aligned}\text{pH} &= \log \frac{1}{C_{\text{H}^+}} = \log \frac{1}{1 \times 10^{-5}} \\ &= \log 1 - \log 1 \times 10^{-5} \\ &= 0 - (-5)\end{aligned}$$

The *pH* is therefore +5 or simply 5. Note that, when the C_{H^+} value is expressed entirely as exponent, such as 1×10^{-5} or $1 \times 10^{-8.26}$, the *pH* values ($\text{pH} = 5$ or $\text{pH} = 8.26$) are directly the exponents with the sign changed. This follows from the meaning or definition of *pH* and the relationship between exponents and logarithms. Interconversion of *pH* values and C_{H^+} values thus are made readily without recourse to a table of logarithms, provided the significant value of C_{H^+} is incorporated in the exponential value. However, when the value of C_{H^+} is given partly in the coefficient and partly in the exponent, logarithm tables are necessary.

Example 4. What is the *pH* value of a solution having a C_{H^+} value of 2.6×10^{-4} ?

Since the *pH* value is the logarithm of the reciprocal of the C_{H^+} value, we have

$$\begin{aligned}\text{pH} &= \log \frac{1}{C_{\text{H}^+}} \\ &= \log \frac{1}{2.6 \times 10^{-4}}\end{aligned}$$

$$\begin{aligned}
 &= \log 1 - \log 2.6 \times 10^{-4} \\
 &= \log 1 - (\log 10^{-4} + \log 2.6) \\
 &= 0 - \log 10^{(-4+0.42)} \\
 &= -\log 1 \times 10^{-3.58} \\
 &= 3.58
 \end{aligned}$$

QUESTIONS AND PROBLEMS—SET 8. pH VALUES

- Define a neutral, a basic and an acidic solution in terms of hydrogen-ion concentration and in terms of pH. What data are necessary to calculate the hydrogen-ion concentration of an acidic or basic solution? Describe two methods by which C_{H^+} or pH may be experimentally measured.
- Give the modification of the Nernst equation as applied to the determination of C_{H^+} and pH, explaining each factor. What is meant by K_w ?
- Identify each of the following solutions, as to whether they are acidic, basic or neutral.

H^+ Ion Concentration		
(a) $1 \times 10^{-8.76}$		Ans. (a) Basic
(b) $2.5 \times 10^{-4.82}$		(b) Acidic
(c) $1 \times 10^{-3.96}$		(c) Acidic
(d) $1 \times 10^{-12.38}$		(d) Basic
(e) $1 \times 10^{-7.41}$		(e) Basic

- What is (a) the hydrogen-ion and (b) the hydroxyl-ion concentration, of a $0.01 M$ solution of $\text{HC}_2\text{H}_3\text{O}_2$ which is ionized 4.17 per cent? $K_w = 1 \times 10^{-13.92}$
- What is (a) the hydrogen-ion and (b) the hydroxyl-ion concentration in a liter of $0.1 M \text{ NH}_4\text{OH}$ which is 1.31 per cent ionized? $K_w = 1 \times 10^{-13.92}$
- Calculate the C_{OH^-} and C_{H^+} of $0.01 M$ solutions of the following acids and bases, the degree of ionization being given. $K_w = 1 \times 10^{-13.92}$

Solution	Per Cent Ionized
(a) HCl	97.2
(b) $\text{HC}_2\text{H}_3\text{O}_2$	4.17
(c) NaOH	93.3
(d) NH_4OH	4.07

- Calculate the hydrogen-ion and hydroxyl-ion concentrations of the following acids and bases, the molarity in each case being 0.1. $K_w = 1 \times 10^{-14}$

Solution	K_{ion}	C_{H^+}	C_{OH^-}
(a) HNO_2	5×10^{-4}	Ans. (a) 8.0×10^{-3}	1.5×10^{-12}
(b) HCHO_2	2×10^{-4}	(b) 4.5×10^{-3}	$2. \times 10^{-12}$
(c) HCN	7×10^{-10}	(c) 1.0×10^{-5}	1.2×10^{-9}
(d) NH_4OH	1.75×10^{-5}	(d) 9.2×10^{-12}	1.3×10^{-3}

8. Designate the molarity with respect to and nature of the HCl or NaOH solutions whose hydrogen-ion concentrations are given below, assuming complete ionization in each case. K_w may be approximated as 1×10^{-14} .

- (a) 1×10^{-2}
- (b) 1×10^{-14}
- (c) 1×10^{-11}
- (d) 1×10^{-3}

9. Calculate the C_{H^+} and C_{OH^-} in solutions of $HC_2H_3O_2$, having the molarities and degrees of ionization designated below.

<i>Molarity</i>	<i>Per Cent Ionized</i>	C_{H^+}	C_{OH^-}
(a) 1.0	0.40	Ans. (a) 4.0×10^{-3}	3.0×10^{-12}
(b) 0.1	1.34	(b) 1.3×10^{-3}	9.2×10^{-12}
(c) 0.01	4.17	(c) 4.2×10^{-4}	2.3×10^{-11}
(d) 0.001	11.7	(d) 1.2×10^{-4}	1.0×10^{-10}

10. Calculate the C_{H^+} and C_{OH^-} ion solutions of NH_4OH , having the molarities and degrees of ionization designated below.

<i>Molarity</i>	<i>Per Cent Ionized</i>
(a) 1.0	0.40
(b) 0.1	1.31
(c) 0.01	4.07
(d) 0.001	11.7

11. What are the *pH* values of solutions having the following designated hydrogen-ion concentrations?

(a) $1 \times 10^{-3.61}$	Ans. (a) 3.61
(b) $1 \times 10^{-7.86}$	(b) 7.86
(c) $1 \times 10^{-12.32}$	(c) 12.32
(d) $1 \times 10^{-5.20}$	(d) 5.20
(e) $1 \times 10^{-2.00}$	(e) 2.00

12. Solutions having the following specified hydroxyl-ion concentrations have what C_{H^+} and *pH* values? $K_w = 1 \times 10^{-13.92}$

OH^- <i>Ion Concentration</i>
(a) 1×10^{-2}
(b) 8×10^{-5}
(c) $1 \times 10^{-7.2}$
(d) $1 \times 10^{-7.87}$
(e) $1 \times 10^{-12.50}$

13. What are the *pH* values of solutions having the following designated hydrogen-ion concentrations?

(a) $2.5 \times 10^{-7.00}$	Ans. (a) 6.60
(b) $3.7 \times 10^{-12.00}$	(b) 11.43
(c) $8.5 \times 10^{-3.56}$	(c) 1.63
(d) $4.5 \times 10^{-8.10}$	(d) 7.45
(e) $7.8 \times 10^{-6.00}$	(e) 5.11

14. What are the *pH* values of solutions having the following designated hydroxyl-ion concentrations? $K_w = 1.0 \times 10^{-13.92}$

- (a) $1 \times 10^{-8.71}$
- (b) $1 \times 10^{-10.00}$
- (c) $1 \times 10^{-7.20}$
- (d) $1 \times 10^{-3.50}$
- (e) $1 \times 10^{-12.00}$

15. What are the *pH* values of 0.1 *M* monoprotic acids, having the designated ionization constants?

K_{ion}

- (a) 5×10^{-4}
- (b) 2×10^{-4}
- (c) 1.8×10^{-5}
- (d) 7×10^{-10}

Ans. (a) 2.30
 (b) 2.35
 (c) 2.87
 (d) 5.00

16. What are the *pH* values of the following solutions of NH_4OH ?

Molarity *Per Cent Ionized*

(a)	1.0	0.40
(b)	0.1	1.31
(c)	0.01	4.07
(d)	0.001	11.7

17. What are the hydroxyl-ion concentrations of the solutions whose *pH* values are specified below? $K_w = 1 \times 10^{13.92}$

pH Value

- (a) 3.25
- (b) 8.97
- (c) 10.00
- (d) 11.27

Ans. (a) 2.14×10^{-11}
 (b) 1.12×10^{-5}
 (c) 1.20×10^{-4}
 (d) 2.24×10^{-3}

18. At what *pH* value will ZnS be prevented from precipitating if the solution contains 0.001 gram ion of Zn^{++} per liter? $K_{\text{s.p.}}$ of $\text{ZnS} = 1.2 \times 10^{-23}$ and $(C_{\text{H}^+})^2 \times C_{\text{S}^-} = 1.1 \times 10^{-23}$.

19. How much NH_4Cl , 85 per cent ionized, should be added to a liter of 1.0 *M* NH_4OH to maintain a *pH* value of 9.25? $K_{\text{ion}} 1.75 \times 10^{-5}$

Ans. 53.4 grams per liter

20. How much $\text{NaC}_2\text{H}_3\text{O}_2$ should be added to a 0.01 *M* $\text{HC}_2\text{H}_3\text{O}_2$ solution so that a *pH* value of 6.20 will be maintained? $\text{NaC}_2\text{H}_3\text{O}_2$ is 80 per cent ionized.

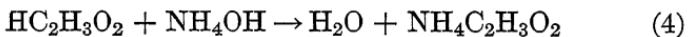
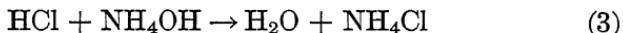
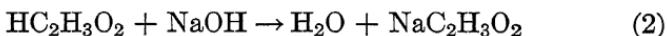
CHAPTER VII

THE THEORY OF NEUTRALIZATION AND HYDROLYSIS. THE ANIONS OF GROUPS II AND III

Thus far we have considered the substance water merely as a solvent and as an effective ionization medium, in which dissolved electrolytes are more or less dissociated into their respective ions. Except in those cases where water has entered into the formation of a new compound, as in the production of sulfuric and nitric acids by reaction of the anhydride oxides with water and in the production of NH_4OH from NH_3 and H_2O , the only function of water thus far considered has been its use in the preparation of aqueous solutions and as a medium in which ionic reactions take place. The interaction of the ions of water with the ions of added solutes and reagents brings into consideration some very important equilibrium relationships, the mathematical treatment of which constitutes the subject matter of the present chapter.

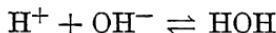
NEUTRALIZATION REACTIONS

Consider the four neutralization reactions:



The reaction of the acid with the base in each instance produces water and the salt of the acid and base. In view of the molecular form in which these equations are written here, one might conclude that these reactions run absolutely to completion. This would be true if it were possible to conduct them in the dry state and to remove the water formed in the reactions. But, since these reactions take place in aqueous solutions, the molecular representation is entirely inadequate and, in fact, misleading. It is important to consider here the ionic relationships.

From an ionic point of view and by virtue of the equilibrium between H^+ ions and OH^- ions, it is impossible for any neutralization reaction to go absolutely to completion. The water equilibrium constant, $K_w = 1.2 \times 10^{-14}$, must be satisfied. This means that, when final equilibrium is reached in a neutralization reaction, there remain in the solution such concentrations of H^+ ions and OH^- ions that their product is 1.2×10^{-14} . The fundamental ionic reaction is the union of H^+ ions and OH^- ions,



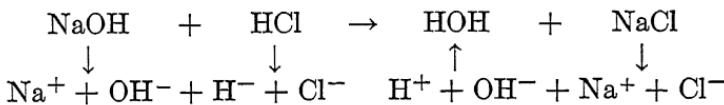
the reaction proceeding from left to right until the relationship,

$$C_{\text{H}^+} \times C_{\text{OH}^-} = 1.2 \times 10^{-14}$$

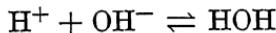
is reached.

The question of neutrality also is involved. Is the solution always strictly neutral when equilibrium is reached? In other words, is it possible theoretically to neutralize equivalent amounts of various acids by various bases? (A neutral solution is, by definition, one in which the H^+ and OH^- ion concentrations are both 10^{-7} .) This question can be answered by a consideration of the strength (degree of ionization) of the acid and base entering into the reaction.

Neutralization of a Strong Acid by a Strong Base. In reaction (1), the HCl , NaOH and NaCl are strong electrolytes and are almost completely ionized in dilute solutions; the water formed is, of course, very weakly ionized. The ionic relationships are shown by the scheme:



As a first approximation, if we consider both the NaOH and the HCl to be completely ionized at the start of the reaction, whatever may be the concentrations of H^+ and OH^- present at the moment the reagents are mixed, the reaction will proceed according to the simple equation,

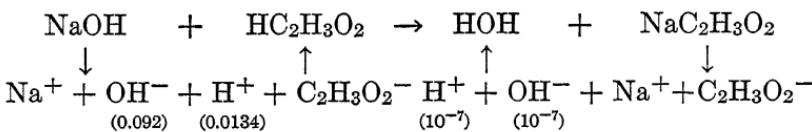


and come to an equilibrium when $K_w = 1.2 \times 10^{-14}$ is reached. Then the C_{H^+} and C_{OH^-} remaining in equilibrium must be equal to each other, and both must have the value 10^{-7} . Since the water

in which the acid and base are dissolved has H^+ and OH^- ion concentrations of exactly 10^{-7} , the net effect of mixing the acid and base is to leave concentrations of 10^{-7} for both H^+ and OH^- . The *pH* value of the resulting salt solution is 7.

We conclude, therefore, that, in the neutralization of a strongly ionized acid by a strongly ionized base, if the acid is as strongly ionized as the base, exact neutrality will be attained, and the reaction lacks 10^{-7} gram ion of H^+ ion and 10^{-7} gram ion of OH^- ion of going to absolute completion.

Neutralization of a Weak Acid by a Strong Base. If, in reaction (2) we bring into reaction in a liter of solution 0.1 gram mole of $\text{HC}_2\text{H}_3\text{O}_2$, 1.34 per cent ionized, and 0.1 gram mole of NaOH , 92 per cent ionized, the initial concentration of H^+ is 0.1×0.0134 or 0.00134 and that of OH^- is 0.1×0.92 or 0.092. The ionic scheme at the start of the reaction is



As the reaction proceeds and H^+ ions (as well as OH^- ions) are used up, more and more non-ionized acetic acid (as well as NaOH) becomes ionized. But, in the weak acid, the ionization constant must be satisfied at all times, and the relationship,

$$\frac{C_{\text{H}^+} \times C_{\text{C}_2\text{H}_3\text{O}_2^-}}{C_{\text{HC}_2\text{H}_3\text{O}_2}} = 1.8 \times 10^{-5}$$

must be fulfilled. The equilibrium,

$$C_{\text{H}^+} \times C_{\text{OH}^-} = 1.2 \times 10^{-14}$$

also must be maintained. When final equilibrium is attained, some non-ionized $\text{HC}_2\text{H}_3\text{O}_2$ must be present to satisfy the acetic acid equilibrium. This lowers the concentration of free H^+ ions and leaves an excess of OH^- ions. Equilibrium thus is reached in a basic solution. The solution will have a *pH* value of more than 7. This has an important bearing on the question of hydrolysis and is referred to later.

The conclusion therefore is that, if the acid is less strongly ionized than the base, the reaction will come to equilibrium in a basic solution.

Neutralization of a Strong Acid by a Weak Base. In reaction (3) the strongly ionized HCl, reacting with the weakly ionized NH₄OH, will establish equilibrium in a solution which is acidic. By analogous reasoning, from reaction (2), the weak base in reaction (3) ties up OH⁻ ions and leaves an excess of H⁺ ions when the joint equilibria,

$$\frac{C_{\text{NH}_4^+} \times C_{\text{OH}^-}}{C_{\text{NH}_4\text{OH}}} = 1.75 \times 10^{-5}$$

and

$$C_{\text{H}^+} \times C_{\text{OH}^-} = 1.2 \times 10^{-14}$$

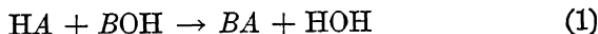
are satisfied.

In general, if the base is weaker than the acid, the neutralization reaction stops in a solution which contains a C_{H⁺} greater than that of C_{OH⁻}. Such a solution will have a pH value of less than 7.

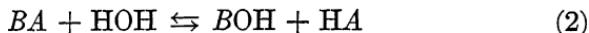
Neutralization of a Weak Acid by a Weak Base. In such a pair, as illustrated by the reaction between HC₂H₃O₂ and NH₄OH, 3 equilibrium constants must be satisfied, namely, the ionization constants of the weak acid and of the weak base and of K_w (the water constant). Whether or not the resulting solution will be neutral depends upon the relative magnitude of the ionization constants; this in turn depends upon the ionizing strength of the acid and the base. If the acid is exactly as weak as the base, both constants are numerically equal, and the final solution will be strictly neutral with a C_{H⁺} of 10⁻⁷. Such a condition is reached approximately when equivalent amounts of HC₂H₃O₂ react with NH₄OH. If the acid is weaker than the base, equilibrium will be reached in a basic solution, one in which the C_{H⁺} is less than 10⁻⁷. Conversely, if the base is the more weakly ionized, the final C_{H⁺} will be greater than 10⁻⁷.

HYDROLYSIS OF SALT SOLUTIONS

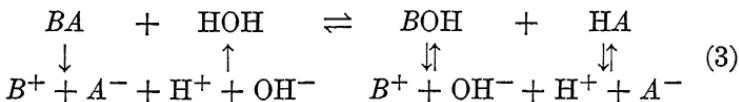
The conclusions reached in regard to the equilibria attained in neutralization reactions can be verified by a consideration of the reactions of hydrolysis. The phenomenon of hydrolysis may be regarded as the reverse of neutralization in which the ions of water react with the ions of the salt produced by the neutralization. Thus the general neutralization reaction between the acid, HA, and the base, BOH,



forming water and the salt, BA , reaches an equilibrium as a result of the hydrolysis reaction,



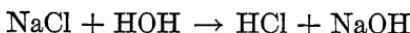
in which the salt reacts with water to form acid and base. Regarded from the standpoint of hydrolysis, equations (1) and (2) can be combined into a single reversible reaction, as shown in equation (3), to which the ionic equilibria are attached.



An examination of this scheme will reveal that, if the cations B^+ have any marked tendency to unite with OH^- ions, a more or less weakly ionized base, BOH , will form, or, if the anions A^- have a marked tendency to unite with H^+ ion, a more or less weakly ionized acid, HA , will form; in either event the ions of water, OH^- and H^+ , reacts with the ions B^+ and A^- , and the reaction proceeds from left to right; that is, hydrolysis takes place. The extent to which the solution is hydrolyzed and the acidic or basic nature of the solution depend upon the type of the salt undergoing hydrolysis.

In keeping with the four types of neutralization reactions already discussed, four types of salts will be considered. Using, as examples, the salts produced in the reactions given on page 260, we shall take up in turn the hydrolysis of solutions containing respectively $NaCl$, $NaC_2H_3O_2$, NH_4Cl and $NH_4C_2H_3O_2$.

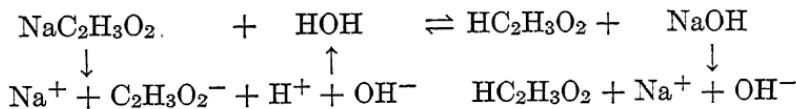
Hydrolysis of a Solution of a Salt Formed by Neutralization of a Strong Acid by a Strong Base. $NaCl$ is an example of a salt of this type. This, like most salts, is highly ionized, whereas water is but slightly ionized. The equation expressing any tendency of a $NaCl$ solution to be hydrolyzed would be expressed by



The products of the hydrolysis, HCl and $NaOH$, are likewise highly ionized. If it is assumed, as a first approximation, that $NaCl$, $NaOH$ and HCl are completely ionized, the net effect will be no reaction or hydrolysis whatsoever. In other words, there will be no tendency for sodium ions to unite with OH^- ions nor for H^+ ions to unite with Cl^- ions. The concentrations of H^+ , OH^- , Na^+ and Cl^- in this instance remain unaltered, and there is no hydrolysis.

To consider this case more exactly, suppose the solution of NaCl is 0.1 *M*, and at this dilution the solute is ionized 92 per cent. At the start there are present 0.092 gram ion of Na⁺ and of Cl⁻ ion, and 10⁻⁷ gram ion of H⁺ ion and OH⁻ ion, per liter of solution. If it were possible for complete hydrolysis to take place, there would be formed 0.1 *M* solutions of HCl and of NaOH, both of which are about 92 per cent ionized. One might suppose that there would be present then in the non-ionized condition HCl and NaOH to the extent of 0.008 gram mole. These, however, would further dissociate as fast as H⁺ and OH⁻ ions were used up. The equilibrium finally reached is expressed by the relation $C_{H^+} \times C_{OH^-} = 1.2 \times 10^{-14}$, and, since both acid and base are equally strongly ionized, the concentrations of H⁺ ion and OH⁻ ion are numerically equal and have the value 10⁻⁷. The *pH* of this solution is 7. The solution is neutral, and hydrolysis is negligibly small.

Hydrolysis of a Solution of a Salt Formed by Neutralization of a Weak Acid by a Strong Base. Sodium acetate is a salt of this type, having been formed from HC₂H₃O₂, a weak acid, and NaOH, a strong base. An aqueous solution of NaC₂H₃O₂, at the moment of preparation, contains a high concentration of Na⁺ ion and C₂H₃O₂⁻ ion and 10⁻⁷ gram ion of H⁺ and OH⁻ ions.



There is a tendency for acetate and hydrogen ions to unite to form the slightly ionized HC₂H₃O₂, but there is little or no tendency for Na⁺ ions and OH⁻ ions to unite. In the formation of non-ionized acetic acid the concentration of H⁺ ions is lowered. This disturbs the water equilibrium; more water ionizes to restore equilibrium; H⁺ ions are used up, at the same time that OH⁻ ions accumulate in the solution. This causes the solution to become basic.

The questions naturally arise: To what extent are hydrogen ions used up? In other words, to what extent does the hydrolysis reaction proceed? How much non-ionized acetic acid forms? What causes the reaction to come to equilibrium? And finally, how basic does the solution become, that is, what are the OH⁻ ion and H⁺ ion concentrations at equilibrium?

If we remember that weak electrolytes are characterized by definite ionization constants, in which the equilibrium between the ions and the non-ionized portion of the weak electrolyte must be satisfied, it follows that, in this case, the relationship,

$$\frac{C_{\text{H}^+} \times C_{\text{C}_2\text{H}_3\text{O}_2^-}}{C_{\text{HC}_2\text{H}_3\text{O}_2}} = K_{\text{ion}} = 1.8 \times 10^{-5}$$

must be maintained as well as the equilibrium,

$$C_{\text{H}^+} \times C_{\text{OH}^-} = K_w = 1.2 \times 10^{-14}$$

Two equilibrium constants must be satisfied, the H^+ ion concentration maintaining equilibrium, on the one hand with acetate ions and non-ionized acetic acid and on the other hand with hydroxyl ions. Hydrolysis will cease when both constants are satisfied.

Dividing in the manner here shown,

$$\frac{\frac{C_{\text{H}^+} \times C_{\text{OH}^-}}{C_{\text{H}^+} \times C_{\text{C}_2\text{H}_3\text{O}_2^-}}}{C_{\text{HC}_2\text{H}_3\text{O}_2}} = \frac{K_w}{K_{\text{ion of HC}_2\text{H}_3\text{O}_2}} = K_{\text{hydrolysis}}$$

gives the expression,

$$\frac{C_{\text{OH}^-} \times C_{\text{HC}_2\text{H}_3\text{O}_2}}{C_{\text{C}_2\text{H}_3\text{O}_2^-}} = \frac{K_w}{K_{\text{ion}}} = K_{\text{hydrolysis of Na}_2\text{CH}_3\text{O}_2}$$

The symbol $K_{\text{hydrolysis}}$ is the hydrolysis constant of the salt. Note that it is the ratio of the water constant and the ionization constant of the acid, and that it depends upon the concentrations of OH^- ions and $\text{C}_2\text{H}_3\text{O}_2^-$ ions and that of the non-ionized $\text{HC}_2\text{H}_3\text{O}_2$. The general formula for the hydrolysis of a salt of this type is given by the expression:

$$\frac{C_{\text{OH}^-} \times C_{\text{non-ionized acid}}}{C_{\text{anion}}} = K_{\text{hydrolysis}}$$

Example 1. Calculate the hydrolysis constant of a 0.1 M solution of $\text{NaC}_2\text{H}_3\text{O}_2$.

Since the constant is the ratio of K_w to K_{ion} for $\text{HC}_2\text{H}_3\text{O}_2$, we have

$$\frac{K_w}{K_{\text{ion}}} = \frac{1.2 \times 10^{-14}}{1.8 \times 10^{-5}} = 6.7 \times 10^{-10}$$

The hydrolysis constant of $\text{NaC}_2\text{H}_3\text{O}_2$ is therefore 6.7×10^{-10} .

The equation,

$$\frac{C_{\text{OH}^-} \times C_{\text{HC}_2\text{H}_3\text{O}_2}}{C_{\text{C}_2\text{H}_3\text{O}_2^-}} = \frac{K_w}{K_{\text{ion}}} = 6.7 \times 10^{-10}$$

enables one to calculate the concentration of $\text{HC}_2\text{H}_3\text{O}_2$ and the OH^- ion concentration, as well as the extent to which hydrolysis has proceeded, provided we know the molarity of the salt solution undergoing hydrolysis. Since the salt is practically completely ionized, and the portion hydrolyzed is extremely small, the concentration of $\text{C}_2\text{H}_3\text{O}_2^-$ ions may be taken as the molarity of the salt. Furthermore, the OH^- ion concentration, in such a solution, is equal to the concentration of the acid formed by hydrolysis.

Example 2. Calculate the OH^- ion concentration in a 0.1 M solution of $\text{NaC}_2\text{H}_3\text{O}_2$ which has undergone hydrolysis, if complete ionization of the solute is assumed.

The equilibrium expressed by the equation,

$$\frac{C_{\text{OH}^-} \times C_{\text{HC}_2\text{H}_3\text{O}_2}}{C_{\text{C}_2\text{H}_3\text{O}_2^-}} = 6.7 \times 10^{-10}$$

must be satisfied.

If we let x equal the concentration of OH^- present at equilibrium, as well as the concentration of $\text{HC}_2\text{H}_3\text{O}_2$ formed during hydrolysis, by substituting in the formula, the total concentrations obtained are

$$\frac{x \times x}{(0.1 - x)} = 6.7 \times 10^{-10}$$

Since, however, $(0.1 - x)$, the concentration of $\text{C}_2\text{H}_3\text{O}_2^-$ in equilibrium, is not sensibly different from 0.1, the original concentration of salt, we may say:

$$\frac{x^2}{0.1} = 6.7 \times 10^{-10}$$

$$x^2 = 6.7 \times 10^{-11}$$

$$x = 8.2 \times 10^{-6}$$

The OH^- ion concentration is therefore 8.2×10^{-6} .

Example 3. What is the concentration of $\text{HC}_2\text{H}_3\text{O}_2$ formed by the hydrolysis of a 0.1 M solution of $\text{NaC}_2\text{H}_3\text{O}_2$?

From example 2, the total concentration of $\text{C}_2\text{H}_3\text{O}_2^-$ formed is x . The value of x has been found to be 8.2×10^{-6} . The total concentration of non-ionized $\text{HC}_2\text{H}_3\text{O}_2$ is therefore also 8.2×10^{-6} .

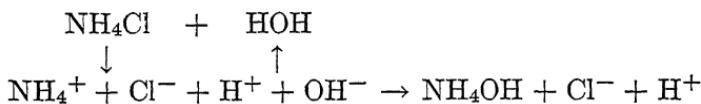
Example 4. To what extent does a 0.1 M solution of $\text{NaC}_2\text{H}_3\text{O}_2$ hydrolyze?

If this solution were completely hydrolyzed, there should be present 0.1 of a gram mole of $\text{HC}_2\text{H}_3\text{O}_2$. Since, as calculated in example 3, the total concentration of $\text{HC}_2\text{H}_3\text{O}_2$ formed is 8.2×10^{-6} , the extent of hydrolysis expressed in terms of percentage is

$$\frac{8.2 \times 10^{-6}}{0.1} \times 100 = 8.2 \times 10^{-3} \text{ per cent}$$

$$= 0.0082 \text{ per cent}$$

Hydrolysis of a Solution of a Salt Formed by Neutralization of a Strong Acid by a Weak Base. In a solution of a salt of this type, NH_4Cl for example, the hydrolysis equilibrium is reached when the ionization constant of the weak base is satisfied as well as that for water. The scheme is



The equilibria leading to the hydrolysis constant are

$$\frac{C_{\text{H}^+} \times C_{\text{OH}^-}}{C_{\text{NH}_4^+} \times C_{\text{OH}^-}} = \frac{K_w}{K_{\text{ion of NH}_4\text{OH}}}$$

which, by division, gives

$$\frac{C_{\text{H}^+} \times C_{\text{NH}_4\text{OH}}}{C_{\text{NH}_4^+}} = \frac{K_w}{K_{\text{ion}}} = K_{\text{hydrolysis}}$$

In general, for any salt of this character

$$\frac{C_{\text{H}^+} \times C_{\text{non-ionized base}}}{C_{\text{cation}}} = K_{\text{hydrolysis}}$$

Hydrolysis of a Solution of a Salt Formed by Neutralization of a Weak Acid by a Weak Base. Ammonium acetate is an example of a salt of this type. For fulfillment of equilibrium, three constants must be satisfied, namely: those of water, of acetic acid and of NH_4OH . The hydrolysis equilibrium is formulated thus:

$$\frac{C_{\text{H}^+} \times C_{\text{OH}^-}}{C_{\text{H}^+} \times C_{\text{C}_2\text{H}_3\text{O}_2^-} \times \frac{C_{\text{OH}^-} \times C_{\text{NH}_4^+}}{C_{\text{NH}_4\text{OH}}}} = \frac{K_w}{K_{\text{acid}} \times K_{\text{base}}}$$

If we divide,

$$\frac{C_{\text{HC}_2\text{H}_3\text{O}_2} \times C_{\text{NH}_4\text{OH}}}{C_{\text{C}_2\text{H}_3\text{O}_2^-} \times C_{\text{NH}_4^+}} = \frac{K_w}{K_{\text{acid}} \times K_{\text{base}}} = K_{\text{hydrolysis}}$$

In general, for salts of this type the equation is

$$\frac{C_{\text{non-ionized acid}} \times C_{\text{non-ionized base}}}{C_{\text{anion}} \times C_{\text{cation}}} = K_{\text{hydrolysis}}$$

In those cases where K_{acid} differs somewhat from K_{base} , yet both represent weakly ionized electrolytes, the hydrogen-ion concentration can be calculated by means of the formula:

$$C_{\text{H}^+} = \sqrt{\frac{K_w \times K_{\text{acid}}}{K_{\text{base}}}}$$

QUESTIONS AND PROBLEMS—SET 9. NEUTRALIZATION AND HYDROLYSIS

1. Define neutralization; define hydrolysis; explain the relation between these two phenomena. What is the relation between the extent of ionization of the parent acid or base and the extent of hydrolysis of a salt?

2. Specify the nature of the solution, whether acidic, basic or neutral which results when the following salts are dissolved in water:

- (a) KNO_3
- (b) $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$
- (c) NH_4CN
- (d) Na_2S

3. State whether equilibrium will be reached in an acid, basic or neutral solution, when equivalent quantities of the following pairs are allowed to react. Write the equations.

- (a) HCN and NaOH
- (b) HNO_2 and NH_4OH
- (c) H_2SO_4 and NH_4OH
- (d) HNO_3 and NH_4OH
- (e) HCHO_2 and KOH

<i>Ans.</i>	(a) Basic
	(b) Acid
	(c) Acid
	(d) Acid
	(e) Basic

4. What volume of 0.1 M NaOH solution is required to react with 10.0 ml. of:

- (a) 0.10 M H_2SO_4
- (b) 0.010 M H_3PO_4
- (c) 0.030 M $\text{H}_2\text{C}_2\text{O}_4$
- (d) 0.10 M HCHO_2
- (e) 0.020 M H_3PO_4

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5. What volume of 0.1 M H_2SO_4 is required to react with 10.0 ml. of:

- (a) 0.10 M $\text{Ca}(\text{OH})_2$
- (b) 0.10 M NH_4OH
- (c) 0.20 M NaOH
- (d) 0.01 M $\text{Ba}(\text{OH})_2$

- Ans.* (a) 10.0 ml.
- (b) 5.0 ml.
- (c) 10.0 ml.
- (d) 1.0 ml.

6. What weight in grams of each of the following acids would react with a liter of 0.100 M NaOH ?

- (a) H_3PO_4
- (b) $\text{HC}_2\text{H}_3\text{O}_2$
- (c) H_2SO_4
- (d) $\text{H}_2\text{C}_2\text{O}_4$
- (e) HCN

7. From the values K ion of $\text{HC}_2\text{H}_3\text{O}_2 = 1.8 \times 10^{-5}$ and $K_w = 1.2 \times 10^{-14}$, calculate the hydrolysis constant of $\text{KC}_2\text{H}_3\text{O}_2$.

$$\text{Ans. } 6.7 \times 10^{-10}$$

8. (a) From the equilibrium expressions, K ion of NH_4OH and K_w for water, derive the equilibrium expression for the hydrolysis of a strongly ionized ammonium salt such as NH_4Cl . (b) From the constants K (NH_4OH) = 1.75×10^{-5} and $K_w = 1.2 \times 10^{-14}$, calculate the hydrolysis constant for NH_4Cl .

9. (a) From the equilibrium expression, K (ion of HCHO_2) and K_w for water, derive the equilibrium expression for the hydrolysis of a strongly ionized formate as NaCHO_2 . (b) Calculate the hydrolysis constant for this salt using K ion of $\text{HCHO}_2 = 2 \times 10^{-4}$ and $K = 1.2 \times 10^{-14}$.

$$\text{Ans. } 6 \times 10^{-11}$$

10. Derive an expression for the hydrolysis constant of a salt of a weak acid and a weak base. Calculate the hydrolysis constant for a salt such as NH_4CHO_2 . (K ion of $\text{HCHO}_2 = 2 \times 10^{-4}$, K ion of $\text{NH}_4\text{OH} = 1.75 \times 10^{-5}$, and $K_w = 1.0 \times 10^{-13.92}$)

11. What is the hydrolysis constant for NaNO_2 ? ($K_w = 1.2 \times 10^{-14}$, K ion of $\text{HNO}_2 = 5 \times 10^{-4}$)

$$\text{Ans. } 2.4 \times 10^{-11}$$

12. Calculate the hydrolysis constants for the following salt solutions, using 0.1 M solutions.

(a) NH_4NO_2	K ion of $\text{NH}_4\text{OH} = 1.75 \times 10^{-5}$
(b) $\text{KC}_2\text{H}_3\text{O}_2$	K ion of $\text{HNO}_2 = 5 \times 10^{-4}$
(c) NH_4CN	K ion of $\text{HC}_2\text{H}_3\text{O}_2 = 1.8 \times 10^{-5}$
(d) KNO_2	K ion of $\text{HCN} = 7 \times 10^{-10}$

13. From the hydrolysis constant of $\text{NaC}_2\text{H}_3\text{O}_2$, 6.7×10^{-10} calculate the H^+ ion concentration in a 0.10 M solution of the salt.

$$\text{Ans. } 1.46 \times 10^{-9}$$

14. Calculate (assuming complete ionization of the salts) the hydrogen-ion concentration in 0.1 M solutions of:

(a) Sodium formate	K ion of $\text{HCHO}_2 = 2 \times 10^{-4}$
(b) Sodium cyanide	K ion of $\text{HCN} = 7 \times 10^{-10}$
	$K_w = 1.2 \times 10^{-14}$

15. Calculate the OH^- ion concentration in a liter of 0.1 M NH_4Cl .

$$\text{Ans. } 1.4 \times 10^{-9} \text{ gram ion}$$

16. Calculate the *pH* value of a 0.1 *M* solution of potassium acetate.

17. To what extent is a solution of 0.1 *M* ammonium chloride hydrolyzed?
Ans. 0.0083 per cent

18. A 0.01 *M* solution of $\text{NaC}_2\text{H}_3\text{O}_2$ is 89.4 per cent ionized. What concentration of $\text{HC}_2\text{H}_3\text{O}_2$ is produced during the hydrolysis of this salt?

19. Calculate the degree (in terms of percentage) to which the following salt solutions are hydrolyzed.

- Sodium formate
- Sodium cyanide
- Ammonium formate
- Ammonium cyanide

20. If you mix 500 ml. of 0.1 *M* HCl and 500 ml. of 0.1 *M* NH_4OH , what is the resulting *pH* of the solution?

GROUP II, THE BARIUM NITRATE GROUP: SULFATE ($\text{SO}_4^{=}$), CHROMATE ($\text{CrO}_4^{=}$)

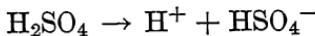
To this group belong the sulfate and the chromate ions. They are precipitated by the group reagent, $\text{Ba}(\text{NO}_3)_2$, as BaSO_4 and BaCrO_4 . The separation of this group depends on the facts: (1) that the ions of group I have been precipitated and removed as insoluble calcium salts, (2) that BaSO_4 and BaCrO_4 are insoluble, and (3) that the barium salts of the ions of succeeding groups are soluble.

SULFATE, $\text{SO}_4^{=}$

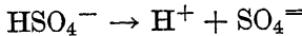
Sulfuric acid is the most important of all acids, indeed, if not the most important of all chemicals, and is used in vast quantities in the chemical industries. As the student knows, it is manufactured by both the contact and the lead chamber processes. It is formed by the reaction of its anhydride, SO_3 , with water:



Concentrated sulfuric acid, as ordinarily dispensed in the laboratory, contains about 95 per cent H_2SO_4 and has a specific gravity of about 1.84. It ionizes almost completely in its first stage of ionization and forms the bisulfate (or acid sulfate) ion:



The bisulfate ion is weakly ionized:



Sulfates and bisulfates are formed by complete or partial neutralization of the acid.

Most of the sulfates of the metals are soluble in water, the exceptions being BaSO_4 , SrSO_4 and PbSO_4 . CaSO_4 , Ag_2SO_4 and Hg_2SO_4 are somewhat insoluble. The table on page 82 gives the solubilities of BaSO_4 , SrSO_4 and CaSO_4 in water. The most important of these is BaSO_4 . It is precipitated as a white finely crystalline solid, very insoluble in water, the solubility being 0.0023 gram per liter. It is practically insoluble in dilute acids.

The formation of BaSO_4 and its insolubility in dilute acids are the most characteristic properties of the sulfate ion and constitute its most important analytical reaction. The barium salts of group I, as well as BaCrO_4 , are soluble in HCl and other strong acids. If BaSO_4 is boiled with Na_2CO_3 , a considerable part of the precipitate undergoes a metathetical reaction in which the constituent ions exchange partners. That is, BaSO_4 is transformed into BaCO_3 , while the $\text{SO}_4^{=}$ and Na^+ ions are in solution as ionized Na_2SO_4 . The reaction may be shown by the equation:

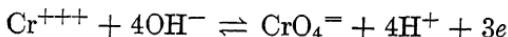


Fusion with solid Na_2CO_3 is a more effective method of accomplishing the same effect. This is, in fact, a general method of rendering soluble many relatively insoluble substances and is applied specifically to the preparation of anion solutions for systematic analysis, as well as for the purpose of removing interfering cations. Attention already has been directed to this property in the discussion of carbonates and is referred to again under the procedure for making the prepared anion solution, page 330.

The formation of basic mercuric sulfate has been made the basis of a sulfate test. This procedure consists of placing a small amount of the solid salt in a watch glass, adding a drop of the reagent (made by mixing 10 grams of mercuric acetate or nitrate and 1 ml. of HNO_3 in 100 ml. of water), and gently warming. A yellow coloration on the surface shows the presence of sulfates. This test may be modified by placing a drop of the reagent on black filter paper and adding a drop of the test solution.

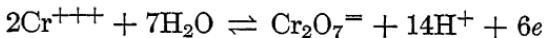
CHROMATE, $\text{CrO}_4^{=}$ AND $\text{Cr}_2\text{O}_7^{=}$

When the chromic ion, Cr^{+++} , is oxidized in an alkaline medium, as was done with Na_2O_2 in the cation procedure, the chromate ion is formed,



the identification of chromium being based on tests for the chromate ion.

If the oxidation of Cr^{+++} takes place in the presence of acid the dichromate ion is produced:



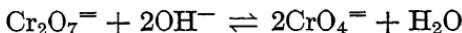
The existence of chromium in both cation and anion forms is already familiar to the student. The section on "Chromium," page 124, should be reviewed at this time.

The orthochromite ion, CrO_3^- and the metachromite ion, CrO_2^- , are formed when the amphoteric hydroxide $\text{Cr}(\text{OH})_3$ is treated with NaOH . In these anions and in the corresponding acids the chromium has a valence of +3.

Chromic acid, H_2CrO_4 , does not exist free in an aqueous solution, but, on ionizing, yields the bichromate ion, HCrO_4^- and the CrO_4^- ion. Chromates such as K_2CrO_4 are derived from chromic acid. Dichromates are salts of dichromic acid, $\text{H}_2\text{Cr}_2\text{O}_7$. If a solution of a chromate, such as the K_2CrO_4 test solution, is acidified, the color changes from yellow to reddish orange, showing the formation of the dichromate, Cr_2O_7^- ion; the reaction is



Conversely, if a dichromate solution is made alkaline, the chromate ion is produced and predominates in the solution:

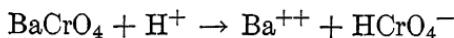


In both the chromate and the dichromate ion, the apparent valence of the chromium is +6, and the predominance of one or the other forms depends solely on the hydrogen-ion concentration.

Potassium chromate and potassium dichromate are two very important reagents. The latter is used extensively in quantitative analysis as an oxidizing agent. The dichromate cleaning solution often recommended is made by dehydrating $\text{K}_2\text{Cr}_2\text{O}_7$ with concentrated H_2SO_4 ; the red crystals in the cleanser are chromic oxide, CrO_3 , a vigorous oxidizer. K_2CrO_4 is used as a test reagent for barium and lead.

From an analytical standpoint, the most important chromate is BaCrO_4 . This forms when the group reagent, $\text{Ba}(\text{NO}_3)_2$, is

added to a chromate-containing solution. BaCrO_4 is soluble in dilute HCl, and thus is distinguished from BaSO_4 . The reaction with HCl is



which forms the bichromate ion. If the acid solution containing dissolved BaCrO_4 is treated with $\text{NaC}_2\text{H}_3\text{O}_2$, the H^+ ion concentration is repressed, and BaCrO_4 is reprecipitated. This is an instance of common-ion effect and already has been applied in the cation scheme for the separation of barium and chromium and lead. The reprecipitation of BaCrO_4 constitutes the simplest test for the presence of chromates.

A further test is that with hydrogen peroxide and is carried out as described under "Chromium," page 124.

The chromate ion is a strong oxidizing agent, especially when in acid medium, where it is present as the Cr_2O_7^- ion and reacts energetically with a considerable number of reducing ions. This property must be taken into account in the analysis of samples containing chromates or dichromates, not only in the anion scheme, but also in the detection of cations. In particular, H_2S would be rapidly oxidized and destroyed in the precipitation of group II of the cations, if precautions were not taken to remove chromates and dichromates prior to precipitation.

Oxidizing action, in general, increases with increasing acidity and is minimized in an alkaline solution. Hence, in order to lessen *redox* reactions, with the consequent destruction of reducing anions, samples for anion analysis containing chromates together with reducing ions must be kept alkaline with $\text{Ca}(\text{OH})_2$ in the procedure of analysis.

PRELIMINARY EXPERIMENTS

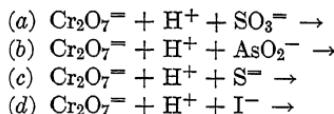
1. Test for the Sulfate Ion. To a few drops of the sulfate test solution, add a few drops of $\text{Ba}(\text{NO}_3)_2$. Write the equation. Acidify the solution containing the precipitate with dilute HCl, and note whether the BaSO_4 is soluble in the acid.

2. Reactions of the Chromate Ion. Acidify a few drops of the chromate test solution. Account for the change of color, and write the equation. Neutralize, and then make the solution alkaline with NaOH. Note the reversal of color. Write the reversible equation for the changes.

Precipitate some BaCrO_4 , and treat the precipitate with dilute HCl. Add a little sodium acetate, and note the effect. Write the equations.

REVIEW EXERCISES

1. In what respect does BaSO_4 differ from most barium salts? On this basis, give the special mode of procedure by which sulfates are detected.
2. Show by equations how H_2CrO_4 and H_2CrO_7 ionize. Also show the relation between CrO_4^- and Cr_2O_7^- by suitable equations involving H^+ and OH^- .
3. What further test might be made for chromates other than the precipitation of yellow BaCrO_4 ? If a solution of a chromate is acidified, what results?
4. The dichromate ion, in an acid medium, is a fairly strong oxidizing agent. To show this effect, complete and balance the following equations:



5. If a sample of material contains a chromate or dichromate and is subjected to the cation procedures, show by equations the chemical changes undergone. If a cation analysis of a sample shows the presence of chromium, what further information will an anion analysis yield regarding the form in which chromium may have been present?
6. If a solution contains the same concentration of SO_4^- and CrO_4^- ions, which will begin to precipitate first, BaCrO_4 or BaSO_4 ? What will be the ratio of the concentration of the one to the other anion, when both salts are present in the precipitate? *Hint:* Fractional precipitation.

OUTLINE OF METHOD OF ANALYSIS OF THIS GROUP

The two ions of this group are readily precipitated by $\text{Ba}(\text{NO}_3)_2$, as BaSO_4 and BaCrO_4 . Usually, it is well to make a separate test for sulfates by first acidifying a few drops of the solution with HCl and then adding a few drops of the group reagent. Under these circumstances only BaSO_4 will precipitate. However, here this step is unnecessary, and the group reagent may be added directly. After complete precipitation, the precipitate is acidified, whereupon BaSO_4 remains as a residue; from this solution BaCrO_4 can be precipitated by the addition of $\text{NaC}_2\text{H}_3\text{O}_2$.

TABLE XXI

DIAGRAMMATIC OUTLINE OF ANALYSIS OF GROUP II

Solution	Precipitate	Residue
SO_4^-	$\underline{\text{BaSO}_4}$	$\underline{\text{BaSO}_4}$ white
$\left[\begin{array}{l} \text{Add} \\ \text{Ba}(\text{NO}_3)_2 \end{array} \right]$	$\left[\begin{array}{l} \text{Add} \\ \text{HCl} \end{array} \right]$	$\underline{\text{Solution}}$
CrO_4^-	$\underline{\text{BaCrO}_4}$	CrO_4^-
		Add $\text{NaC}_2\text{H}_3\text{O}_2 \rightarrow \underline{\text{BaCrO}_4}$ yellow

PROCEDURE FOR THE ANALYSIS OF GROUP II

To 1 ml. of the sample, add $\text{Ba}(\text{NO}_3)_2$, dropwise, until precipitation is complete. Centrifuge; if members of group III or succeeding groups are to be tested for in this sample, reserve the centrifugate. Wash the residue, which may consist of BaSO_4 and BaCrO_4 or both, with 8 to 10 drops of water. A white residue is probably BaSO_4 ; if the residue is yellow, both salts may be present.

Treat the residue with 5 drops of dilute HCl, and centrifuge. A white residue remaining after the acid treatment is BaSO_4 and is the final test for sulfates.

The centrifugate from the acid treatment will be yellow if chromates are present. This can be confirmed by adding a few drops of $\text{NaC}_2\text{H}_3\text{O}_2$, whereupon the acidity is decreased and yellow BaCrO_4 reprecipitates. As a still further confirmation, the peroxide test can be made (see page 126 for details).

GROUP III. THE ZINC NITRATE GROUP:

SULFIDE (S^-), CYANIDE (CN^-), FERROCYANIDE, $[\text{Fe}(\text{CN})_6]^{4-}$.

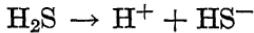
FERRICYANIDE, $[\text{Fe}(\text{CN})_6]^{3-}$

In a systematic analysis, these 4 anions, whose calcium and barium salts in general are soluble, are precipitated with zinc nitrate in the form of ZnS , $\text{Zn}(\text{CN})_2$, $\text{Zn}_3\text{K}_2[\text{Fe}(\text{CN})_6]_2$ and $\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$. The first 3 anions are reducing agents; the last is an oxidizing substance.

SULFIDE, S^-

Many of the important metals are found in nature as sulfide ores, notably the ores of copper, lead and zinc. The student already has become familiar with the properties of many metallic sulfides, as well as with the parent acid, H_2S .

Sulfides and bisulfides (or hydrosulfides) are the salts of hydro-sulfuric acid, H_2S , better known as hydrogen sulfide. This gas, with which the student is familiar, is slightly soluble in water, forming, at room temperatures, a 0.1 M solution of the diprotic weakly ionized acid. The ionization in water takes place according to the equations,

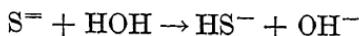


and



yielding H^+ , HS^- and S^- ions.

The sulfides and bisulfides of the alkali metals and alkaline earths are soluble and undergo hydrolysis while being formed, since they are the salts of a weak acid and strong bases. For example, the test solution, Na₂S, reacts with water to form the bisulfide ion,



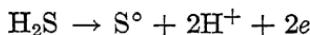
rendering the solution strongly alkaline. The HS⁻ ion undergoes further hydrolysis yielding H₂S:



It is on this account that Al(OH)₃ and Cr(OH)₃ are precipitated, rather than Al₂S₃ and Cr₂S₃, from an alkaline sulfide solution.

Since calcium and barium sulfide are soluble, the sulfide ion is not precipitated in group I or II. ZnS, however, is precipitated with the Zn(NO₃)₂ reagent in this group.

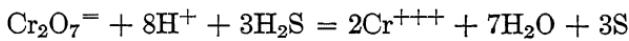
Hydrogen sulfide and acidified solutions of soluble sulfides are strong reducing agents and are readily oxidized by oxidizing agents, generally to free sulfur:



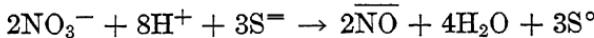
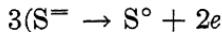
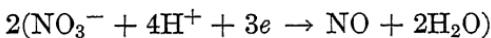
or



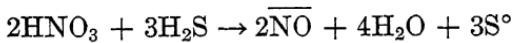
Thus, K₂Cr₂O₇ is reduced to chromic ion, the equation for the reaction being



KMnO₄ is reduced to manganous ion. Nitric acid is reduced to NO, with either the formation of sulfur or complete oxidation of the sulfide ion to SO₄⁼. In the first case we have, as electron reactions,



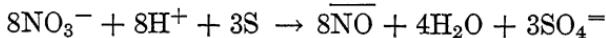
or, expressed in molecular form,



The oxidation of the sulfide ion to the sulfate ion is shown by the electron equation,



which, when combined with the equation for the reduction of the NO_3^- ion, gives

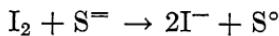


or, expressed in molecular form,

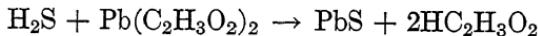


Toward sulfurous acid or acidified solutions of sulfites, H_2S acts as a reducing agent. The main product of the reaction is free sulfur; the sulfite ion is reduced to S; and the sulfide ion is oxidized to free sulfur. The reaction has been referred to under "Sulfites," page 240.

The reduction of iodine by H_2S is an important analytical reaction; it is used in the quantitative determination of sulfides and of H_2S :



Two tests for sulfides are recommended in the systematic procedure. One is based on the fact that a strip of moistened lead acetate paper becomes dark brown or black when exposed to H_2S :



owing to the formation of lead sulfide.

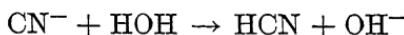
The other is based on the violet-red color produced by sodium nitroprusside, $\text{Na}_2\text{Fe}(\text{CN})_5\text{NO}$, when treated with an alkaline solution of a sulfide. This is a very sensitive test for the sulfide ion, but it is not given by gaseous H_2S . A similar result is produced by this reagent with sulfites.

CYANIDE, CN^-

Cyanides and the free acid, gaseous HCN, are violent poisons. It is recommended that cyanides be omitted from elementary courses. If, however, they are to be included, due precautions should be taken against their dangerous character. All experiments which involve the liberation of gases with materials suspected of containing cyanides should be carried out under a hood, and extreme caution should be taken.

The cyanide ion readily forms a number of complex ions as, for example, the complex silver, copper and cadmium ions previously referred to in the discussion of the properties of these metals and the ferrocyanide and ferricyanide ions included in this group. The ease with which these complexes are formed often serves as a test for cyanides. Zn(CN)₂ is white and fairly insoluble.

Acidification of a cyanide solution results in the liberation of gaseous HCN which has a characteristic odor of bitter almonds. Its aqueous solution is very weakly ionized; in fact it is weaker than carbonic acid. Soluble cyanides are extensively hydrolyzed,



rendering the solution strongly alkaline. This accounts for the fact that solid soluble cyanides give off the odor of HCN.

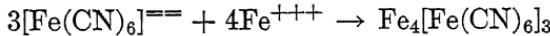
KCN is a fairly good reducing agent being oxidized to cyanogen gas according to the reaction: CN⁻ → CN + 1e.

It reduces, for example, cupric ion to cuprous ion.

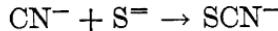
The cyanide ion can be converted to the ferrocyanide ion by treatment in an alkaline medium with FeSO₄ solution. The ferrous hydroxide formed by the action of OH⁻ on Fe⁺⁺ further reacts to give ferrous cyanide, Fe(CN)₂. This dissolves in an excess of the cyanide solution to form the ferrocyanide ion:



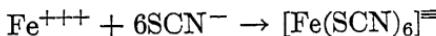
This property is used as a test for cyanides, by further adding a solution of FeCl₃, which produces a heavy blue precipitate of ferric ferrocyanide (Prussian blue):



The cyanide ion is oxidized to the thiocyanate ion by action of ammonium polysulfide:



This property may be employed as a test for cyanides. As described in the following, after acidification, a drop or two of FeCl₃ will produce the deep red color of the ferric thiocyanate complex:



If a strip of filter paper is moistened with ammoniacal copper nitrate solution and held in a stream of H₂S to precipitate CuS,

allowed to dry, and then touched with a drop of cyanide solution, there will be formed $[\text{Cu}(\text{CN})_3]^{=}$, leaving a clear spot on the paper. The spot covered by the drop should be compared with the rest of the paper, which serves as a blank. Addition of NH_4OH to an unknown solution will prevent the formation of precipitates of ferrocyanides, ferricyanides and thiocyanates, if these ions are present in the solution.

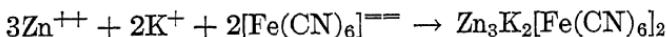
A strip of filter paper, dipped into a saturated aqueous solution of picric acid and then into a solution of Na_2CO_3 , and finally treated with a drop of cyanide solution and dried, will show a red or red-brown color. Sulfides give a somewhat similar color.

FERROCYANIDE, $[\text{Fe}(\text{CN})_6]^{=}$

Ferrocyanic acid, $\text{H}_4\text{Fe}(\text{CN})_6$, is a white solid, soluble in water, unstable and easily oxidized in the air. The potassium salt, $\text{K}_4\text{Fe}(\text{CN})_6$, is an important analytical reagent. With the exception of the alkali and alkaline earth salts, all ferrocyanides are insoluble in water; however double salts of the alkali and alkaline earth elements, such as $\text{CaK}_2\text{Fe}(\text{CN})_6$, are insoluble in water. Soluble ferrocyanides are yellow in color; a number of the insoluble ones are white, but most of them are colored.

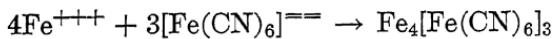
Ferrocyanides are mild reducing agents and are oxidized to ferricyanides by oxidizing agents, such as $\text{K}_2\text{Cr}_2\text{O}_7$, KMnO_4 , Br_2 and H_2O_2 . On heating or on treatment with concentrated H_2SO_4 , they are decomposed into a variety of products, such as CO , CO_2 , HCN and NH_3 .

The ferrocyanide ion reacts with many different cations to form insoluble products. With the Zn^{++} ion and $\text{K}_4\text{Fe}(\text{CN})_6$, there is formed the salt, zinc potassium ferrocyanide, according to the equation:



Ferrous salt solutions, such as FeSO_4 , react at first a light-colored precipitate of $\text{K}_2\text{Fe}[\text{Fe}(\text{CN})_6]$ which quickly oxidizes in the air to Prussian blue, $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$.

On the other hand, ferric salt solutions react directly to form Prussian blue:



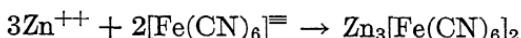
This reaction, it will be recalled, is used as a test for the ferric ion. See, in this connection, the reactions of iron on page 117.

FERRICYANIDE, $[Fe(CN)_6]^{6-}$

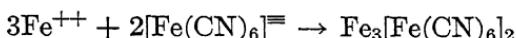
Ferricyanic acid, $H_3Fe(CN)_6$, is a brown solid, soluble in water. With bases it yields stable salts known as ferricyanides. With the exception of the alkali metal and alkaline earth salts, these salts are insoluble in water.

The ferricyanide ion is a strong oxidizing agent and is reduced to ferrocyanide by a number of reductants, even in alkaline solution. Thus the sulfide, arsenite, sulfite, iodide, and so forth, are apt to be destroyed in mixtures containing the ferrocyanide ion.

With $Zn(NO_3)_2$, the ferricyanide ion forms zinc ferricyanide:



Ferrous ions produce Turnbull's blue (ferrous ferricyanide), $Fe_3[Fe(CN)_6]_2$:



Ferric ions yield a brown soluble product, $Fe[Fe(CN)_6]$. For more detail concerning the reactions of iron with ferrocyanides and ferricyanides, see pages 116 and 117.

PRELIMINARY EXPERIMENTS

1. Action of Group Reagent. Label 4 centrifuge tubes, S^- , CN^- , $[Fe(CN)_6]^{6-}$ and $[Fe(CN)_6]^{4-}$, respectively. Place 3 drops of test solution of the respective anions in the tubes. To each tube, add, dropwise, the group reagent 0.5 M $Zn(NO_3)_2$ until precipitation is complete. Centrifuge each tube. Write the equations.

2. Tests for Sulfide Ion. (a). Moisten a strip of lead acetate test paper, and, holding it over the mouth of the tube containing the ZnS , add a drop or two of dilute HCl. What do you observe taking place in the tube and on the paper? Give the equations for the reactions taking place.

(b) To a drop of sulfide test solution on the spot plate, add a drop of NaOH and then one of sodium nitroprusside. Make a note of the resulting color. Does H_2S give this test?

3. Test for Cyanide Ion. To the tube containing the $Zn(CN)_2$, add 1 ml. of water to make a suspension. Treat a piece of filter or drop-reaction paper with NaOH and hold over the mouth of the tube. Add a drop of dilute HCl to the suspension, and heat the tube in the water bath to boiling for about 1 minute. (*Caution: Do not hold your face over the tube.*) Then treat the exposed section of the paper with a drop of freshly prepared $FeSO_4$ solution, acidify the spot with a tiny drop of concentrated HCl and finally add a drop of $FeCl_3$ reagent. To what is the blue color due? Explain the reactions which have taken place.

4. Test for Ferrocyanide Ion. To 2 drops of $K_4Fe(CN)_6$ test solution, add a few drops of $FeCl_3$ reagent. What is the precipitate? Write the equation.

Repeat the experiment, using a few drops of freshly prepared FeSO_4 solution.

5. Test for Ferricyanide Ion. Repeat the two experiments under paragraph 4, using $\text{K}_3\text{Fe}(\text{CN})_6$ test solution. Tabulate the results, showing the action of Fe^{++} ion and Fe^{+++} ion on ferrocyanide and ferricyanide ion. Correlate these experiments with the tests for both forms of iron (page 116).

REVIEW EXERCISES

- What reagents, other than a lead salt solution, might one use to produce a black stain as a test for a sulfide? What would produce a yellow stain? An orange stain?
- The sulfide ion is a vigorous reducing agent. How might it react with the dichromate ion in an acidified solution? Show the result as a balanced equation.
- Give formulas showing the composition of the complex ions which the CN^- ion forms with Ag^+ , Cu^{++} , Cd^{++} , Fe^{++} and Fe^{+++} . Look up the instability constants for these complex ions.
- What happens when the ferrocyanide ion is treated with Fe^{++} ? With Fe^{+++} ? When the ferricyanide ion is treated with Fe^{++} ? With Fe^{+++} ?
- The $K_{s.p.}$ of ZnS is 1.2×10^{-23} . In order to initiate the formation of ZnS in a solution which contains 10 milligrams of S^- per milliliter, what concentration of Zn^{++} ion is required?

OUTLINE OF METHOD OF ANALYSIS OF THIS GROUP

On account of the strong oxidizing nature of the ferricyanide ion, many reducing ions will be oxidized by this ion; it cannot be present with the three reducing ions of this group and is best excluded completely from student samples. The group precipitate, consisting of ZnS , $\text{Zn}(\text{CN})_2$, $\text{Zn}_3\text{K}_2[\text{Fe}(\text{CN})_6]_2$ or, separately, $\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$, is divided into several portions, and each ion is tested for separately.

The test for the sulfide ion depends upon the formation of a metallic sulfide, for which PbS is chosen. The cyanide test involves the formation of Prussian blue. Likewise, ferrocyanides are tested for with FeSO_4 , resulting in the formation of Prussian blue. Ferricyanides, if to be tested for, are detected with FeCl_3 , forming Turnbull's blue.

TABLE XXII

DIAGRAMMATIC OUTLINE OF ANALYSIS OF GROUP III

Solution	Precipitate	Use Separate Portions
S^-	ZnS	$-\text{HCl} + \text{PbAc}$ paper $\rightarrow \text{PbS}$ black
CN^-	$\text{Zn}(\text{CN})_2$	$-\text{NaOH}$ on paper + $\text{HCl} + \text{FeSO}_4 + \text{FeCl}_3$ $\rightarrow \text{Fe}_4[\text{Fe}(\text{CN})_6]$ blue
$[\text{Fe}(\text{CN})_6]^{--}$	$\text{Zn}_3\text{K}_2[\text{Fe}(\text{CN})_6]_2$	$-\text{HCl} + \text{FeCl}_3 \rightarrow \text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ blue
$[\text{Fe}(\text{CN})_6]^{=}$	$\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$	$-\text{HCl} + \text{FeSO}_4 \rightarrow \text{Fe}_3[\text{Fe}(\text{CN})_6]_2$ blue

PROCEDURE FOR ANALYSIS OF GROUP III

Since the ferricyanide ion is such a strong oxidizing agent, even in an alkaline medium, that the sulfide ion of this group and certain reducing ions of other groups are destroyed by it, it is best that this offender be excluded from all samples. No particular difficulty is experienced in the detection of the remaining 3 ions.

Preliminary Group Test. To a few drops of the sample or of the centrifugate from the removal of group II, add a few drops of zinc nitrate. If a precipitate forms, the sulfide, the cyanide or the ferrocyanide ion is present.

Group Precipitation. If this preliminary test shows the presence of group III, add slowly, while stirring, the group reagent, 0.5 M zinc nitrate, until precipitation is complete. The precipitate may consist of ZnS , $\text{Zn}(\text{CN})_2$, or $\text{Zn}_3\text{K}_2[\text{Fe}(\text{CN})_6]_2$.

Detection of Sulfide. Remove a small amount of the group precipitate to another test tube, treat it with a drop of HCl, and hold in the mouth of the tube a strip of wet lead acetate paper. If the test paper darkens, sulfides are present in the sample.

Detection of Ferrocyanide. Remove another small portion of the group precipitate to the spot plate, acidify with a drop of dilute HCl, and add a drop of FeCl_3 . A blue color (Prussian blue) shows the presence of the $[\text{Fe}(\text{CN})_6]^{4-}$ ion.

Detection of Ferricyanide. To another portion of the precipitate acidify with a drop of dilute HCl, and then add a drop of freshly prepared solution of FeSO_4 . A blue color shows presence of ferricyanide ion.

Detection of Cyanide. Transfer the remainder of the precipitate to a small flask, add 5 ml. of water, and shake to form a suspension. Treat a piece of filter or reaction paper with NaOH, acidify the suspension with dilute HCl, and place the paper over the mouth of the flask. Heat the contents of the flask to boiling, and continue heating for half a minute. Then treat the filter paper with 2 drops of freshly prepared FeSO_4 solution, acidify the spot with 1 drop of concentrated HCl, and finally add 1 drop of FeCl_3 solution. If a blue color develops, it shows the presence of cyanides.

CHAPTER VIII

THE ANIONS OF GROUPS IV AND V. THE ELECTRO-CHEMICAL THEORY OF OXIDATION

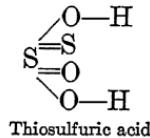
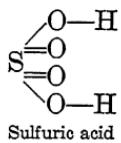
GROUP IV. THE SILVER NITRATE GROUP:

THIOSULFATE ($S_2O_3^-$), THIOCYANATE (SCN^-), IODIDE (I^-),
BROMIDE (Br^-), CHLORIDE (Cl^-)

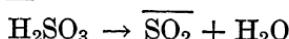
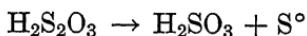
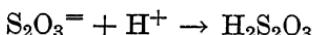
In the systematic scheme here employed for the separation of anions into groups, the anions of groups I, II and III are removed successively by means of calcium, barium and zinc nitrate. Since most silver salts are relatively insoluble, it is important that the ions of these preceding groups be completely precipitated and removed. Advantage then is taken of a solution of $AgNO_3$ to precipitate the ions of this group in the form of $Ag_2S_2O_3$, $AgSCN$, AgI , $AgBr$ and $AgCl$. The $AgNO_3$ used is a 5 per cent solution.

THIOSULFATE, $S_2O_3^-$

Thiosulfates are derived from the hypothetical acid, thiosulfuric acid, $H_2S_2O_3$. This acid may be represented as H_2SO_4 in which one of the oxygen atoms has been replaced by sulfur, as shown by the structural formulas:

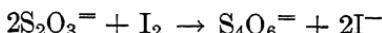


The free acid cannot be isolated, because, when a thiosulfate is treated with an acid, decomposition into H_2SO_3 and S takes place; the final reaction products are sulfur, sulfur dioxide and water. The reactions during decomposition may be shown by the equations:



An acidified solution of a thiosulfate therefore behaves in many respects like sulfurous acid. Hence, certain oxidizing agents, in acidified solutions, react toward the thiosulfate ion in exactly the same way as toward sulfites, since in both cases the sulfurous acid, produced upon acidification, acts as the reducing agent.

The best-known salt is sodium thiosulfate, Na₂S₂O₃, from which the test solution is prepared. The thiosulfate ion is a strong reducing agent. One of the most important analytical reactions is the reduction of iodine with Na₂S₂O₃:

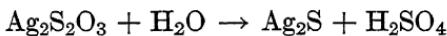


the thiosulfate ion being oxidized to the tetrathionate ion. Na₂S₂O₃ is the "hypo" of the photographer; it is used to dissolve the unreduced portions of the silver halide in the photographic film. In a silver chloride solution, for example, it forms a complex ion:



Many thiosulfates are insoluble in water; in concentrated solutions, calcium and barium thiosulfates are formed, and there is accordingly some possibility of precipitating the thiosulfate ion in groups I and II.

Silver nitrate, the group reagent, precipitates Ag₂S₂O₃, white, when first formed. This quickly undergoes hydrolysis, the reaction probably being



changing color from yellow through brown and finally to black, the color of Ag₂S. For this reason, no specific test for thiosulfates can be made; the detection depends on the formation of the black Ag₂S during the group precipitation.

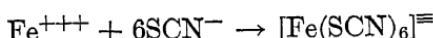
THIOCYANATE, SCN⁻

Thiocyanates are salts of thiocyanic acid, HSCN, which is an unstable gas at ordinary temperatures. This acid is analogous to normal cyanic acid, HO CN, in which sulfur has replaced the oxygen. The structural formula is H—S—C≡N. Frequently the formula, CNS⁻, rather than SCN⁻, is employed to designate this ion; isothiocyanic acid has the formula, H—N=C=S. In aqueous solution HSCN is a strong acid. The salts are colorless, excepting, of course, those containing a colored cation.

Thiocyanates resemble the halides in solubility, AgSCN , $\text{Pb}(\text{SCN})_2$ and $\text{Cu}_2(\text{SCN})_2$ being relatively insoluble, and $\text{Hg}(\text{SCN})_2$ being only slightly soluble. These insoluble salts, however, readily dissolve in an excess of alkali thiocyanate to form complex ions of the type $[\text{Ag}(\text{SCN})_3]^-$, $[\text{Hg}(\text{SCN})_4]^-$, $[\text{Co}(\text{SCN})_6]^{2-}$ and $[\text{Fe}(\text{SCN})_6]^{2-}$. Double salts such as those encountered in one of the characteristic reactions of mercury (see page 176) readily form with metallic ions.

Silver nitrate precipitates curdy white silver thiocyanate, AgSCN , even in a solution strongly acid with dilute HNO_3 . The precipitate is somewhat soluble in dilute ammonia but not in the ammoniacal silver nitrate reagent (Miller's reagent) employed in the procedure of separation.

A very sensitive reaction of the SCN^- ion is the formation of the blood-red complex ion formed with ferric ion:

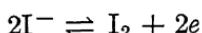


This reaction, it will be recalled, is likewise an extremely delicate test for iron. See, in this connection, page 117. The thiocyanate ion is a mild reducing agent, being oxidized to the CN^- ion.

IODIDE, I^-

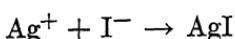
The element iodine, a dark crystalline solid, and the heaviest member of the halogen family, forms a series of acids, of which hydriodic acid, or hydrogen iodide, HI , and iodic acid, HIO_3 , are the most important. Iodides and iodates are derived from these two acids.

The iodide ion, I^- , is a strong reducing agent, easily oxidized to free iodine, I_2 , by a number of oxidizing agents. The electron equation is



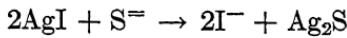
Free iodine and the iodate ion are good oxidizing agents.

Silver iodide is readily formed by the reaction with AgNO_3 :



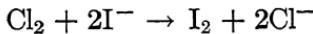
AgI is extremely insoluble in water and acid solvents. Ammonium hydroxide will not dissolve it. In this respect AgI differs from AgCl —a fact utilized in the separation of the iodide ion from the chloride ion. Ammonium polysulfide, however, transposes it into

Ag_2S , the iodide ion being liberated; this property is employed in the systematic scheme of separation. The reaction probably takes place in accordance with the equation:



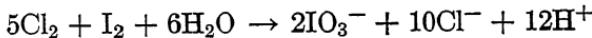
The vigorous reducing action of the iodide ion enables it to be oxidized readily by a large number of oxidizing agents. To show the analogy with bromides and chlorides the action of the following oxidizing agents is described here. (Compare the effects here with those for bromide and chloride.)

1. Chlorine Water. A saturated solution of chlorine in water rapidly oxidizes iodides to free iodine:

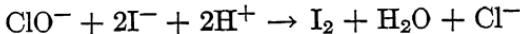


The iodine thus liberated can be dissolved in an organic solvent, such as chloroform or carbon tetrachloride, where it appears as violet in the organic solvent layer. This reaction sometimes is employed as a test for iodides.

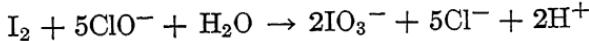
If an excess of chlorine water is used, the iodine is further oxidized to the iodate form:



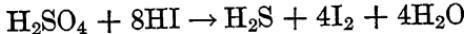
2. Sodium Hypochlorite. This oxidant reacts like chlorine water,



liberating iodine. This is the reagent employed for the detection of iodides in the scheme of analysis. This reagent will further oxidize iodine to iodate in accordance with the equation:

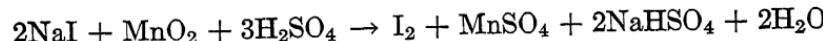


3. Sulfuric Acid. Concentrated H_2SO_4 oxidizes solid iodides with the formation of I_2 , H_2S and S . The first effect is the liberation of HI which then reacts with the H_2SO_4 according to the equation:

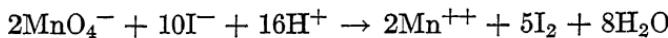


The iodine reacts further with H_2S to give free S .

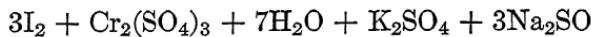
4. Concentrated H_2SO_4 and MnO_2 . The action of this mixture on iodides is like that on bromides and chlorides, liberating iodine:



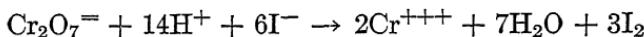
5. *Potassium Permanganate.* In a dilute sulfuric acid solution, iodides reduce KMnO_4 :



6. *Concentrated H_2SO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$.* If a mixture of a solid iodide and solid $\text{K}_2\text{Cr}_2\text{O}_7$ is heated with concentrated H_2SO_4 , iodine is formed. The reaction is expressed by the equation:



Compare this with the corresponding reaction for bromides and chlorides. The same result is obtained when a dilute solution of the test substance is treated with dilute H_2SO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$; the reaction is best expressed in ionic form:

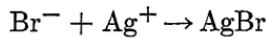


BROMIDE, Br^-

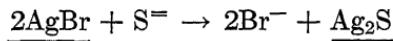
Bromine is a heavy brown liquid. The important acids are hydrobromic acid (an aqueous solution of hydrogen bromide, HBr) and bromic acid, HBrO_3 . The corresponding anions are the bromide, Br^- , and the bromate, BrO_3^- .

Most of the bromides are water soluble, the exceptions being, like the iodides and chlorides, AgBr , PbBr_2 , Hg_2Br_2 and Cu_2Br_2 .

The group reagent, AgNO_3 , precipitates pale yellow AgBr :

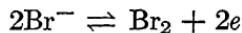


Silver bromide is insoluble in acid solvents. It is transposed by ammonium polysulfide:



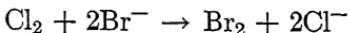
It is only partly soluble in NH_4OH .

The bromide ion is a fairly strong reducing agent, less energetic than the iodide but more so than the chloride ion. The electron reaction is:



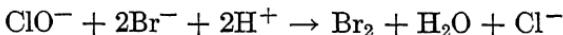
Reactions showing the behavior of a number of oxidizing agents toward the bromide ion are discussed here. These properties should be compared with those of iodides and chlorides.

1. *Chlorine Water.* This reacts toward the bromide ion in the same manner as with iodides, liberating bromine: •



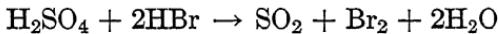
The liberated bromine can be extracted with chloroform or carbon tetrachloride and gives to the organic solvent layer a reddish-yellow color. This is a good test for bromides.

2. *Sodium Hypochlorite.* Bromides are oxidized to bromine by NaClO,

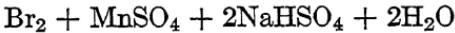
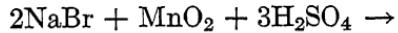


in a solution made acid with dilute H₂SO₄. This method for the identification of bromides is utilized in the scheme of analysis and is outlined as a preliminary experiment.

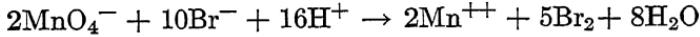
3. *Sulfuric Acid.* Concentrated H₂SO₄ reacts with bromides, first to liberate HBr, which is at once oxidized to bromine:



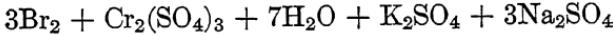
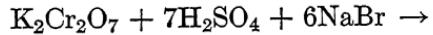
4. *Concentrated H₂SO₄ and MnO₂.* A mixture of solid bromide, MnO₂, and concentrated H₂SO₄, when heated, evolves free bromine. The reaction is analogous to that taking place with chlorides:



5. *Potassium Permanganate.* Bromides will reduce an acidified solution of KMnO₄ with liberation of Br₂:



6. *Concentrated H₂SO₄ and K₂Cr₂O₇.* A mixture of NaBr and solid K₂Cr₂O₇, when treated and warmed with concentrated H₂SO₄, reacts to form bromine, according to the equation:



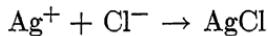
This reaction is similar to that of iodides but differs from that of chlorides.

In a dilute solution of K₂Cr₂O₇, acidified with dilute sulfuric acid, no reaction takes place; in this sense the behavior differs from that of iodides.

CHLORIDE, Cl^-

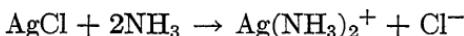
Chlorine is the most widely distributed and most abundant member of the halogen family. It is a gaseous element and forms a series of acids. Hydrochloric acid is the aqueous solution of hydrogen chloride and yields the chloride ion upon neutralization or dissociation. Other acids of chlorine are hypochlorous, chlorous, chloric and perchloric, from which are derived the following ions: hypochlorite, ClO^- ; chlorite, ClO_2^- ; chlorate, ClO_3^- , and perchlorate, ClO_4^- . Provision is made in this book for the detection of chlorides and chlorates. The use of sodium hypochlorite as an oxidizing agent already has been mentioned.

All chlorides are soluble in water with the exception of those of group I of the cations, namely, AgCl , Hg_2Cl_2 and PbCl_2 , along with Cu_2Cl_2 and TlCl . Silver chloride is a curdy white precipitate formed by the simple reaction:



Silver chloride is insoluble in acids but dissolves in ammonia solution, forming with the latter reagent the diammono-silver ion. Silver bromide partially dissolves in ordinary ammonia solutions but silver iodide does not. AgCl is transposed to Ag_2S by $(\text{NH}_4)_2\text{S}_2$.

The test for the chloride ion consists in acidifying, with dilute HNO_3 , the ammonia complex obtained by dissolving AgCl in ammonia solution:



Upon acidification with HNO_3 , silver chloride is precipitated:



This, it will be recalled, is the test for silver also.

Since, however, silver bromide is partly soluble in ammonia and upon acidification would yield AgBr , hardly distinguishable from AgCl , this simple mode of procedure must be modified when mixtures are being analyzed which are known to contain bromides. A specially prepared ammonia solution, known as ammoniacal silver nitrate or Miller's reagent, is used, in which the concentrations of NH_3 and AgNO_3 are so adjusted as to prevent the dissolving of the AgBr in the ammoniacal solvent. The reagent supplied is 0.25 M with respect to NH_4OH , 0.01 M with respect to

AgNO_3 , and contains in addition 0.25 gram mole of KNO_3 per liter; the last ingredient aids in the coagulation of the AgCl . With the use of this reagent, it is found that enough AgCl dissolves to give the chloride test, but not enough AgBr or AgI dissolve to give misleading conclusions.

The effect of oxidizing agents on the chloride ion is compared here with that for bromides and iodides.

1. *Chlorine Water.* Obviously this reagent will have no effect on chlorides.

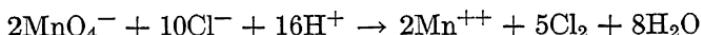
2. *Sodium Hypochlorite.* This reagent likewise has no effect on the chloride ion.

3. *Sulfuric Acid.* Concentrated H_2SO_4 does not oxidize chloride but liberates free HCl when added to a solid chloride such as NaCl .

4. *Concentrated H_2SO_4 and MnO_2 .* When a mixture of MnO_2 and a solid chloride is treated with concentrated H_2SO_4 and heated, chlorine is liberated. The equation for the reaction is

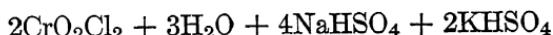


5. *Potassium Permanganate.* Chlorides are oxidized by KMnO_4 in an acidified solution according to the equation,



only, however, when the chloride-ion concentration is high and the solution is hot.

6. *Concentrated H_2SO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$.* Solid $\text{K}_2\text{Cr}_2\text{O}_7$ and concentrated H_2SO_4 react with a solid chloride, such as NaCl , to form chromyl chloride, CrO_2Cl_2 , a vapor which can be distilled and condensed. The reaction proceeds according to the equation:



This is the chromyl chloride test, sometimes employed for the detection of chlorides. The vapors are distilled into NaOH solution, in which the yellow color of the chromate ion which forms can be recognized. This latter reaction can be shown by the equation:



PRELIMINARY EXPERIMENTS

1. Action of Group Reagent. Label 5 centrifuge tubes, respectively, $S_2O_3^{2-}$, SCN^- , I^- , Br^- , and Cl^- . Place 3 drops of the respective test solution in each. To the thiosulfate solution, add a drop of dilute HNO_3 and then several drops of the group reagent, a 5 per cent solution of $AgNO_3$; observe how the precipitate gradually changes color. What is the white and finally the black precipitate? Write the equation by which Ag_2S is formed. What is the test for thiosulfates?

To the other tubes add enough $AgNO_3$ to insure complete precipitation. Note the colors of the precipitates, and write the equations for their formation. Centrifuge, and wash. Try the action of $(NH_4)_2S_2$ on these silver salts, by adding a few drops of the reagent. Write the equations.

2. Test for Thiocyanate. To a tube containing $AgSCN$, add 10 drops of water, shake, and then add a tiny drop of $FeCl_3$ reagent. Account for the color by writing the equation. Compare this result with one of the tests for iron.

3. Oxidation Tests for Iodide and Bromide. (a). To a few drops of iodide test solution, add 5 drops of chloroform, $CHCl_3$, or carbon tetrachloride, CCl_4 , and then add, dropwise, a solution of sodium hypochlorite, $NaClO$. Shake well, and observe how the dark color in the aqueous layer is absorbed and changed in the organic solvent layer. Write the equation by which free I_2 is formed.

Carefully continue the addition of the oxidizing agent until the violet color disappears in the chloroform layer. To what ionic form has the iodine been oxidized? Write the equation.

(b) To another tube containing a few drops of bromide test solution and 5 drops of chloroform, add a drop of dilute H_2SO_4 and then, dropwise, $NaClO$ reagent. Explain the color in the $CHCl_3$ layer. Give the equation for this oxidation.

(c) Take a mixture of iodide and bromide test solutions, and verify the presence of both ions in the same solution by first conducting the iodide test, then destroying the free iodine, and finally by acidifying, obtaining the evidence of the bromide.

4. Action of Ammoniacal $AgNO_3$. Reprecipitate some $AgCl$, $AgBr$ and AgI in original tubes labeled Cl^- , Br^- and I^- , and then add a few drops of Miller's reagent. Explain what happens. What is the function of this reagent? What is in the chloride tube? Acidify the contents of this tube with HNO_3 , and explain what happens.

REVIEW EXERCISES

1. Assemble the equations for the reactions taking place when the anions of this group are precipitated with $AgNO_3$. Write equations for the transposing of AgI , $AgBr$ and $AgCl$ by $(NH_4)_2S_2$.

2. Write equations for the identifying tests for the ions of this group.

3. How do $AgCl$, $AgBr$ and AgI behave, respectively, toward NH_4OH ? Explain the function of Miller's reagent in the separation of chlorides from bromides.

4. Write balanced equations for the interaction of the iodide ion in an acid solution with the following oxidizing ions: (a) $\text{Cr}_2\text{O}_7^{=}$; (b) $\text{AsO}_4^{=}$; (c) MnO_4^- .

5. Show the method of balancing the following equations:

- (a) For iodides: property (2), (5), (6).
- (b) For bromides: property (2), (4), (5).
- (c) For chlorides: property (4), (6).

6. Calculate the concentration of Ag^+ necessary to start precipitation of AgI , AgBr and AgCl , respectively, in test solutions containing 0.01 gram ion of I^- , Br^- , and Cl^- ion per liter.

7. A certain solution is known to contain 1×10^{-2} gram ion of Cl^- and of I^- per liter. Calculate the ratio of C_{Cl^-} to C_{I^-} in the solution when sufficient Ag^+ has been added to produce precipitates of AgI and AgCl . Hint: See "Fractional Precipitation" in Part I.

8. Calculate the C_{Ag^+} in a solution which is 0.1 M with respect to the complex salt $\text{Ag}(\text{NH}_3)_2\text{Cl}$, if complete ionization of the salt is assumed. The instability constant of $\text{Ag}(\text{NH}_3)_2^+$ is 7×10^{-8} .

9. Provide a scheme for the systematic separation and identification of the ions in a mixture containing $\text{AsO}_4^{=}$, $\text{PO}_4^{=}$, $\text{CrO}_4^{=}$, S^- , Cl^- and I^- ions.

10. Supply a scheme for the systematic separation and identification of a mixture of ions consisting of SO_3^- , SO_4^- , S^- , S_2O_3^- , SCN^- ions.

OUTLINE OF METHOD OF ANALYSIS OF THIS GROUP

When the ions of this group are precipitated with AgNO_3 , there will be formed $\text{Ag}_2\text{S}_2\text{O}_3$, AgCNS , AgI , AgBr and AgCl . The silver thiosulfate at once decomposes into Ag_2S which is black; this constitutes the only possible indication of the presence of thiosulfates. The thiocyanate is readily identified with FeCl_3 , forming the deep-red ferric thiocyanate complex ion.

The identification of the iodide and bromide ions depends upon the successive oxidation of I^- to I_2 and then to iodate, by the action of hypochlorite, followed by further acidification and re-

TABLE XXIII
DIAGRAMMATIC OUTLINE OF ANALYSIS OF GROUP IV

<i>Solution</i>	<i>Precipitate</i>			
S_2O_3^-	$\text{Ag}_2\text{S} \rightarrow$ Black ppt. shows S_2O_3^-			
	AgSCN	SCN^- Treat a portion with $\text{FeCl}_3 \rightarrow$		
	$\underline{\text{AgI}}$	$\text{Fe}(\text{SCN})_6^{=}$ red		
I^-	$\underline{\text{AgNO}_3}$ centfg.	Add I^-	CHCl_3	$\text{I}_2 \rightarrow$ violet in CHCl_3
	$\underline{\text{AgBr}}$	$(\text{NH}_4)_2\text{S}_2$	NaClO ,	
Br^-	$\underline{\text{H}_2\text{SO}_4}$ boil	Br^-	then add H_2SO_4	$\text{Br}_2 \rightarrow$ brown in CHCl_3
	centfg.		NaOCl ,	
Cl^-	$\underline{\text{AgCl}}$	Cl^-	then Miller's reagent	$\text{Ag}(\text{NH}_3)_2^+ + \text{Cl}^- + \text{HNO}_3 \rightarrow$ <u>AgCl white</u>

peated action of NaClO whereby the bromide ion is oxidized to free bromine. Both are recognized by the distinctive colors of the free elements in an organic extractant such as chloroform.

The detection of the chloride ion, in the presence of bromide ion, depends upon the use of a specially buffered solution of ammonia in AgNO_3 solution, so regulated that AgCl will dissolve, but AgBr will not. Acidification of the solution containing $\text{Ag}(\text{NH}_3)_2\text{Cl}$ with HNO_3 , resulting in the precipitation of AgCl is the final test for chlorides.

PROCEDURE FOR ANALYSIS OF GROUP IV

Preliminary Group Test. To about $\frac{1}{2}$ ml. of the sample, add the group reagent, a 5 per cent solution of AgNO_3 , until precipitation is complete, and then make the solution just acid with dilute HNO_3 . The presence of a precipitate indicates thiosulfates, thiocyanates, iodides, bromides or chlorides.

Detection of Thiosulfate. If, during the preliminary group test, the precipitate turned dark, passing through color shades of yellow, orange and red to black, the presence of thiosulfates is shown. The color change is due to decomposition of $\text{Ag}_2\text{S}_2\text{O}_3$, the final product being Ag_2S . This effect will be observed again, if thiosulfate is present, during the group precipitation.

Group Precipitation. If, in the preliminary test, a precipitate formed, but the thiosulfate test was negative, treat the entire solution with AgNO_3 reagent until precipitation is complete, and then heat to boiling. Then add very carefully small drops of dilute HNO_3 , with stirring, until the solution is faintly acid toward litmus; avoid an excess. Centrifuge, and wash the residue twice with a few drops of water, and add these washings to the supernatant liquid which is to be reserved for tests for anions of group V. Continue washing the residue until the washings no longer give a precipitate of AgCl with dilute HCl. The residue may contain AgSCN , AgI , AgBr and AgCl .

If, on the other hand, thiosulfates are present, first treat the solution from group III with dilute NH_4OH until alkaline to litmus. Then add a drop in excess. This step is necessary to neutralize the acidity produced by the hydrolysis of silver thiosulfate. Then treat the solution with AgNO_3 reagent until precipitation is complete. Heat to boiling, and then add sufficient dilute HNO_3 to make the solution faintly acid toward litmus, meanwhile stirring as the acid is added. If the solution becomes too acid, there is

danger of interaction of thiosulfate with chlorate ion from group V. Centrifuge, and set aside in another tube the supernatant solution for examination for group V anions. Wash the precipitate twice with a few drops of water, and add these washings to the solution of group V. Repeatedly wash the residue until washings are free from silver ion as tested with dilute HCl. In this residue there may be Ag_2S , AgSCN , AgI , AgBr and AgCl .

Detection of Thiocyanate. Remove a portion of the group precipitate to another test tube, and add a few drops of water and then a drop or two of ferric chloride solution. A red color in the supernatant liquid due to the presence of the complex ion, $\text{Fe}(\text{SCN})_6^{3-}$, identifies thiocyanate.

Detection of Iodide. In order to test for iodides, as well as for bromides and chlorides, the group precipitate must be redissolved. Proceed as follows: Treat the precipitate with 5 drops of ammonium polysulfide, heat to boiling; centrifuge, and again treat with 5 drops of $(\text{NH}_4)_2\text{S}_2$, add dilute H_2SO_4 , and again boil to remove H_2S . Centrifuge, and wash, discarding the residue. The supernatant liquid now can be examined for the presence of the halogen ions.

To a drop of the liquid, made ammoniacal with NH_4OH , add a few drops of chloroform, and then NaClO . Then add dilute $\text{HC}_2\text{H}_3\text{O}_2$, dropwise, and shake the mixture at intervals. If the chloroform layer becomes purple, iodides are present. Continue the addition of the NaOCl until the purple color is discharged.

Detection of Bromide. To the same tube, add a drop of H_2SO_4 , and continue to add more NaClO . In the presence of a bromide a brown color will develop in the chloroform layer.

Detection of Chloride. To 4 or 5 drops of the solution in the polysulfide, add AgNO_3 until the halides again have been precipitated as silver salts. Centrifuge, and treat the residue with 5 drops of ammoniacal silver nitrate (Miller's reagent) which will dissolve only the AgCl . Centrifuge, and to the solution add a drop of dilute HNO_3 . The formation of white AgCl shows the presence of chlorides in the sample.

GROUP V. THE SOLUBLE ANION GROUP: CHLORATE (ClO_3^-), ACETATE ($\text{C}_2\text{H}_3\text{O}_2^-$), NITRITE (NO_2^-), NITRATE (NO_3^-)

Normally, this group includes the chlorate, acetate and nitrite ions. It is designated here as the soluble group, since all the ordinary salts of these anions are rather water-soluble, and in a sys-

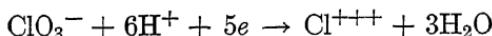
tematic separation the preceding group reagents will have failed to precipitate them as the calcium, barium, zinc and silver salts.

Nitrates are included here for discussion, on account of the similarity with nitrites. Since group reagents have introduced the nitrate ion, this constituent always must be tested for in a separate portion of the original sample.

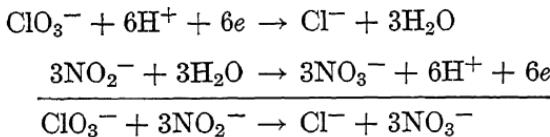
CHLORATE, ClO_3^-

Chlorates are salts of chloric acid. This acid exists only in moderately dilute solutions and is strongly ionized. HClO_3 and chlorates are vigorous oxidizing agents. *Warning: Solid chlorates should never be ground together nor heated with oxidizable substances nor heated with concentrated sulfuric acid, since a reaction may take place with explosive violence.*

All chlorates are soluble in water. Potassium chlorate has been employed, it will be remembered, in conjunction with concentrated HCl as a powerful oxidizing solvent. When this is reduced with concentrated HCl, the change probably takes place in accordance with the equation:



The test for chlorates consists in reducing ClO_3^- to chloride ion. The reducing agent used in the procedure of analysis is NaNO_2 , for which the equation is



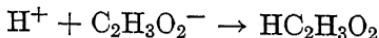
The final test then is the same as for chlorides, namely, the precipitation of AgCl with AgNO_3 in a HNO_3 solution.

Other agents which will reduce chlorates are FeSO_4 , Na_2SO_3 and H_2S .

ACETATE, $\text{C}_2\text{H}_3\text{O}_2^-$

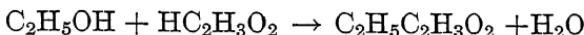
Acetates are salts of acetic acid. The student already has become familiar with this weakly ionized organic acid in connection with the calculation of ionization constants, common-ion effect and buffer action. The formula for the acid is written in organic chemistry as CH_3COOH ; the formula, CH_3COO^- , or the symbol Ac is sometimes used instead of $\text{C}_2\text{H}_3\text{O}_2^-$ to denote the acetate ion.

If a solution containing the acetate ion is acidified with any strong acid, acetic acid will form:



This may be recognized by the vinegar-like odor.

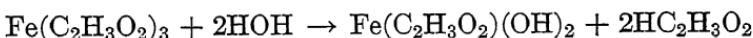
The formation of esters (organic salts) of acetic acid is the basis of a test for acetates. Ethyl alcohol, $\text{C}_2\text{H}_5\text{OH}$, for example, reacts with acetic acid to form the organic ester, ethyl acetate, which possesses a sweet fruity odor. The reaction is:



Instead of ethyl alcohol, some chemists prefer to use amyl alcohol, $\text{C}_5\text{H}_{11}\text{OH}$, the ester formed being amyl acetate, $\text{C}_5\text{H}_{11}\text{C}_2\text{H}_3\text{O}_2$, which has the odor of bananas.

A delicate test for acetates depends upon the precipitation of basic lanthanum acetate and the adsorption of iodine by the precipitate. The test is conducted by treating the acetate solution with $\text{La}(\text{NO}_3)_3$ reagent, dilute iodine solution and finally dilute NH_4OH , until a permanent precipitate remains. An intense blue color, similar to that produced by starch and iodine, forms. This test invariably gives good results when applied to a pure acetate solution, but frequently fails when attempted in systematic analysis.

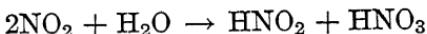
Some basic acetates are insoluble in water. Those of analytical importance are the basic acetates of ferric iron, aluminum and chromium. If, for example, $\text{NaC}_2\text{H}_3\text{O}_2$ is added to a ferric chloride solution, $\text{Fe}(\text{C}_2\text{H}_3\text{O}_2)_3$ will form, coloring the solution red. If the solution then is diluted and boiled, hydrolysis takes place, precipitating basic ferric acetate according to the reaction:



This behavior of ferric ion toward acetates is referred to again under the "Systematic Analysis for Cations," Part III, page 342.

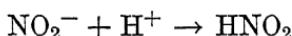
NITRITE, NO_2^-

Nitrites are the salts of nitrous acid. HNO_2 is an unstable weakly ionized acid and is formed when a nitrite is treated with a stronger acid or when NO_2 is passed into water:

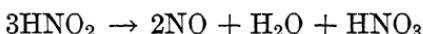


All common nitrites are soluble in water (silver nitrite, however, is only slightly soluble). Some complex nitrites, such as $K_2NaCo(NO_2)_6$, are quite insoluble (recall one of the tests for potassium).

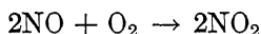
Nitrites are easily decomposed by acids. When a nitrite is treated with dilute acid, such as HCl, the first action is the formation of nitrous acid:



This decomposes into nitric oxide, water and HNO_3 :



As the NO escapes into the air, it is oxidized to brown fumes of NO_2 :

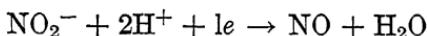


If a strip of starch potassium iodide test paper is held in the escaping fumes, the iodide will be oxidized to I_2 and will color the paper blue.

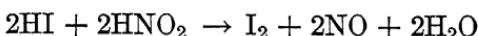
The most important and interesting property of nitrites is that they may act as either reducing or oxidizing agents. Examples of both behaviors are discussed here. When the nitrite ion acts as a reducer, it is oxidized to the nitrate ion,



and when it functions as an oxidizer it is reduced to NO,

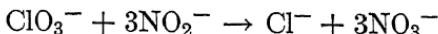


A reaction similar to the effect of NO_2 on starch potassium iodide test paper may be made in nitrite solution by adding a few drops of KI reagent and then acidifying with dilute acetic acid. The reaction that takes place is as follows:



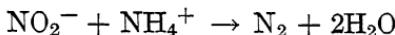
Here the nitrite is the oxidizer and the iodide the reducer. The liberated iodine may be shown by adding a few drops of chloroform or carbon tetrachloride and then shaking. The iodine colors the organic solvent layer an intense violet. Since certain other anions will liberate iodine from iodides, this reaction is not an infallible test for nitrites.

As a reducing agent, NaNO_2 is employed in reducing the chlorate ion to chloride ion:



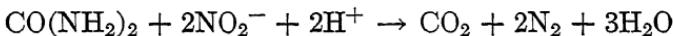
This reaction proceeds only in acid solution; hence chlorates and nitrites are compatible as long as the mixture is not acidified. See "Chlorates," page 296.

The nitrite ion is capable of oxidizing ammonium salts, the products being nitrogen and water:



This reaction may be used to destroy nitrites when the ring test is to be used for the detection of nitrates.

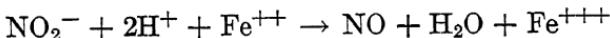
Urea is oxidized and nitrites are reduced, with liberation of free nitrogen, when acidified solutions are allowed to react. The reaction takes place according to the equation:



The evolution of nitrogen observed during the reaction may serve as a test for nitrites. Moreover, the reaction may be employed to remove all but traces of nitrites in conducting the ring test for nitrates.

As previously shown, when nitrites are treated with acids, nitrous acid, as well as nitric acid, forms as one of the products. Dilute acetic acid will bring about this decomposition of a nitrite but, in the case of a nitrate, concentrated sulfuric acid is required. This fact enables one to test for a nitrite in the presence of a nitrate by the so-called ferrous nitrosyl or "ring" test.

This test as applied to nitrites consists of treating the solution with *dilute acetic acid* and then adding a solution of ferrous sulfate. The Fe^{++} ion reduces the nitrous acid formed upon acidification:



The NO then forms the complex ferrous nitrosyl ion which has a brown color:



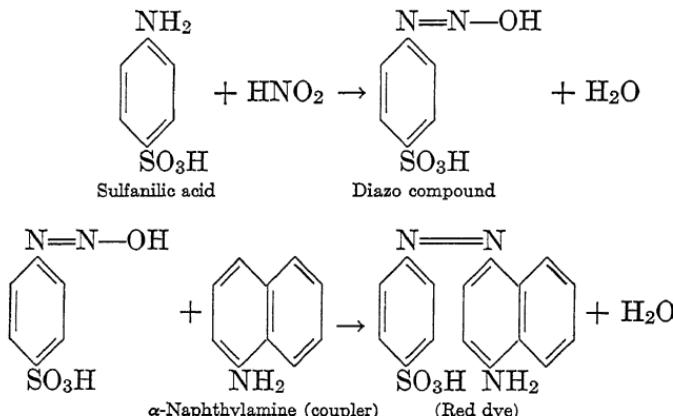
In the case of a nitrite the brown color appears throughout the solution, whereas in the case of a nitrate, when *concentrated* H_2SO_4 instead of $\text{HC}_2\text{H}_3\text{O}_2$ is used, the color appears as a ring at the junction of the two liquids. In applying this test to the detection

of nitrites, provision is made for the removal of anions which otherwise would interfere.

Although NO is the usual product of reduction, it is possible for lower reduction products, for example, N₂O, N₂ or NH₃, to be formed in particular cases.

By the action of HNO₂ on aromatic amines, the so-called diazo compounds are formed. The phenomenon is known as the Griess reaction. If these compounds are "coupled" with suitable compounds, intensely colored dyes result. Since diazo compounds are formed only by HNO₂, such a series of reactions may be used to detect this acid. Several pairs of amines and couplers have been proposed. If, to a drop of test solution acidified with acetic acid, a drop of sulfanilic acid solution is added and then a drop of α -naphthylamine solution, a red color will form immediately or after a short time.

The α -naphthylamine solution must be colorless before the test is conducted (the appearance of a color indicates partial decomposition, and this colored reagent sometimes will give a color with sulfanilic acid alone). The reactions are as follows:

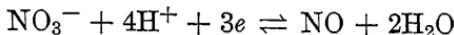


The test may also be carried out with paper impregnated with the two reagents.

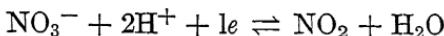
NITRATE, NO₃⁻

The student is already very familiar with the parent substance, nitric acid. The reagent as usually dispensed in the laboratory is the constant-boiling mixture of specific gravity 1.42, containing 69.77 per cent of pure nitric acid by weight. It is a strongly ionized acid and a vigorous oxidizing agent, which yields on reduc-

tion a series of products such as NO_2 , NO , N_2O , N_2 and NH_3 , depending upon the conditions of temperature, concentration and reducing agent present. A dilute solution of HNO_3 , in its function as an oxidizer, is reduced to NO :



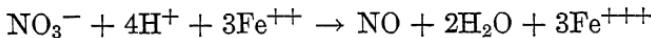
Concentrated HNO_3 , however, is reduced to NO_2 :



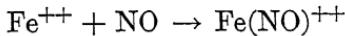
Reactions involving dilute and concentrated HNO_3 already have been encountered in the cation procedures where HNO_3 acid was used as an oxidizing solvent.

All normal nitrates are water-soluble, but some, on dissolving, form insoluble basic salts by hydrolysis: for example, BiONO_3 .

The most important reaction of nitrates from a detection standpoint is the so-called ring test, in which the nitrosyl ferrous complex, $\text{Fe}(\text{NO})^{++}$, is formed. When concentrated H_2SO_4 is added to a nitrate, and then a strong solution of FeSO_4 is carefully supplied, reduction of the NO_3^- takes place, and NO is formed in accordance with the equation:



As in the corresponding test for nitrites, the NO combines with the Fe^{++} ion to form the complex ion:

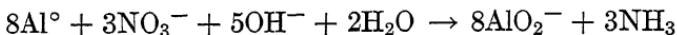


This appears as a dark brown ring at the junction of the two liquids. It is to be noted that nitrites must be removed, by decomposition with NH_4Cl or urea, before the ring test for nitrates is conducted, since nitrites interfere by forming the same complex. However, nitrites can be detected in the presence of nitrates, since the test for the former can be made with acetic acid, whereas that for the latter require concentrated sulfuric acid.

Nitron reagent sometimes is employed to detect nitrates. This reagent, which has the empirical formula $\text{C}_{20}\text{H}_{18}\text{N}_4$, forms in an acid solution an addition product, $\text{C}_{20}\text{H}_{18}\text{N}_4 \cdot \text{HNO}_3$, a white crystalline substance. The reagent is 1, 4-diphenyl-3, 5-endanilodihydrotriazol and has the structural formula $\text{C}_6\text{H}_5-\text{N}-\text{CH}=(\text{NC}_6\text{H}_5)_2=\text{C}=\text{N}$. When dissolved in acetic acid, the reagent is known as "Nitron," and, when in formic acid, "Fornitrol." A number of other anions form insoluble products with the

reagent. In systematic analysis, most of these are removed, including the nitrite. This test is not recommended.

Nitrates are reduced to ammonia by a number of metals, particularly aluminum and zinc, and this property may be utilized as a test for the nitrate ion. In the case of aluminum the reduction proceeds in an alkaline solution according to the equation:



The evolved ammonia then is tested for by litmus paper, as described on page 53. Ammonium salts, of course, must be absent from the solution of the sample when this test for nitrates is made.

PRELIMINARY EXPERIMENTS

Make up a mixture, from the test solutions, consisting of about 5 drops of chlorate, acetate, nitrite and nitrate ions.

1. Test for Chlorate. Take a few drops of the test mixture, add dilute H_2SO_4 until slightly acid, and then a drop or two in excess. To effect the reduction of chlorate to chloride, add a small crystal of sodium nitrite, and heat to boiling. Add to the boiled solution a drop of concentrated HNO_3 and a few drops of AgNO_3 . Write the equation for the reduction of chlorate to chloride. What is the white precipitate formed on the addition of AgNO_3 ?

2. Test for Acetate. Place about $\frac{1}{2}$ ml. of the mixture in a crucible, and add an equal volume of ethyl alcohol and about the same volume of concentrated H_2SO_4 . Warm the mixture and note the fruity odor. What is it? Write the equation. It is advisable to run a control test with the acetate test solution, so that the odors of acetic acid, ethyl alcohol and ethyl acetate can be compared.

3. Test for Nitrite. On a spot plate place a few drops of the mixture, and add a crystal of ferrous sulfate and 2 drops of dilute acetic acid. The brown color of the ferrous nitrosyl ion $[\text{FeNO}]^{++}$ shows the presence of the nitrite. To produce the same brown substance from nitrates requires the use of concentrated H_2SO_4 ; hence this procedure is applicable for nitrites in the presence of nitrates.

4. Test for Nitrate. The ordinary "ring" test for nitrates must be modified in the presence of nitrites. To do this, take about 1 ml. of the solution, place it in a crucible, add a heaping spatulaful of NH_4Cl (or the amount which can be held on the point of a penknife), and, dropwise, add dilute H_2SO_4 until effervescence ceases, and then a few drops in excess. If the volume exceeds about 3 ml., concentrate it by evaporation. Transfer the solution to a centrifuge tube, and cool under the water tap.

The ring test now can be carried out. Place about $\frac{1}{2}$ ml. of the solution, freed from the nitrite by the foregoing procedure, in a test tube, add an equal volume of concentrated H_2SO_4 , cool thoroughly under the tap, and then, with the tube in an inclined position, carefully add a freshly prepared solution of ferrous sulfate. A brown ring, the ferrous nitrosyl ion, will form at the junction of the two liquids.

REVIEW EXERCISES

1. Write an equation for one important reaction of each anion of this group with the required test reagents.
2. What is the apparent valence of chlorine in ClO_3^- , Cl^- , ClO_2^- , ClO^- ?
3. What happens when concentrated HCl is added to a chlorate, such as KClO_3 ? Write the equation. Where was this mixture employed in cation analysis?
4. How can you test for a nitrite in the presence of a nitrate? After studying the following procedure, tell how you would proceed with the detection of nitrate when nitrite also has been shown to be present in the same sample.
5. Under what conditions will the nitrate ion act as an oxidizing agent? What are the products in each case? Write equations showing the function of NO_2^- as an oxidizer and as a reducer.
6. When dilute HNO_3 dissolves a metallic sulfide, the NO_3^- becomes NO ; when concentrated HNO_3 is employed as solvent for a metallic sulfide, the usual product is NO_2 . Write balanced equations illustrating this for the action of dilute and concentrated HNO_3 on PbS .
7. What happens when concentrated HCl is mixed with concentrated HNO_3 ? Write the equation. What is the mixture called? Explain why this mixture is a powerful oxidizing solvent.
8. The ionization constant of $\text{HC}_2\text{H}_3\text{O}_2$ is 1.8×10^{-5} . Would acetic acid be formed in a solution containing $\text{NaC}_2\text{H}_3\text{O}_2$ if an acid more weakly ionized than $\text{HC}_2\text{H}_3\text{O}_2$ were added? Explain why H_2SO_4 will liberate $\text{HC}_2\text{H}_3\text{O}_2$ from acetates.
9. If enough strong acid is added to a solution of $\text{NaC}_2\text{H}_3\text{O}_2$ to produce a molarity of 0.05 with respect to $\text{HC}_2\text{H}_3\text{O}_2$, what is the hydrogen-ion concentration in the test solutions which contains 10 milligrams per milliliter (10 grams per liter)?
10. The test solution of $\text{NaC}_2\text{H}_3\text{O}_2$ has undergone partial hydrolysis, because this salt is the product of the neutralization of a weak acid by a strong base. Calculate the hydroxyl-ion concentration in the test solution which contains 10 grams of $\text{NaC}_2\text{H}_3\text{O}_2$ per liter.
11. Predict the probable result on the precipitation of metallic sulfides in the cation procedures, if acetate ions are present along with cations of groups II and III when adjustment of the acidity is made.
12. Give diagrammatic schemes for the separation and identification of the anions in the following mixtures:
 - (a) $\text{SO}_3^{=}$, $\text{S}^{=}$, CN^- , Cl^- , NO_3^- .
 - (b) AsO_2^- , ClO_3^- , $\text{S}^{=}$, I^- , $\text{CrO}_4^{=}$.
 - (c) $\text{PO}_4^{=}$, $\text{AsO}_4^{=}$, Cl^- , Br^- , NO_2^- , NO_3^- .

OUTLINE OF METHOD OF ANALYSIS OF THIS GROUP

The chlorate, acetate and nitrite ions are identified in separate portions of the solution constituting this group. Chlorates are reduced to the chloride ion and then identified as AgCl . Acetates are best detected by the odor of one of its organic salts, namely

ethyl acetate. The nitrite is tested for through the formation of the brownish-colored ferrous nitrosyl complex, $\text{Fe}(\text{NO})^{++}$, in an acetic acid solution.

The nitrate ion, however, in a systematic analysis, is tested for in a portion of the original sample, because, through the use of the group reagents, this ion will have been introduced into the solution. The so-called ring test here employed is interfered with by the presence of certain other anions. The removal of the interfering ions of other groups is brought about by their precipitation with barium acetate and silver acetate. The interfering chloride ion is reduced, and interfering nitrite is eliminated by evaporation with urea. In the resulting solution, the nitrate then is detected by the use of ferrous sulfate and concentrated H_2SO_4 , producing the familiar "ring" test.

TABLE XXIV

DIAGRAMMATIC OUTLINE OF ANALYSIS OF GROUP V

Solution	
ClO_3^-	Treat centfg.
$\text{C}_2\text{H}_3\text{O}_2^-$	from IV with Na_2CO_3 ,
NO_2^-	evaporate to small vol.,
NO_3^-	centf., wash, use separate portions
	ClO_3^- : add $\text{H}_2\text{SO}_4 + \text{NaNO}_2$, then $\text{AgNO}_3 \rightarrow \text{AgCl}$
	$\text{C}_2\text{H}_3\text{O}_2^-$: add $\text{C}_2\text{H}_5\text{OH} + \text{conc. H}_2\text{SO}_4 \rightarrow \text{C}_2\text{H}_5\text{C}_2\text{H}_3\text{O}_2$, fruity odor
	NO_2^- : add dil. $\text{HC}_2\text{H}_3\text{O}_2 + \text{FeSO}_4 \rightarrow \text{Fe}(\text{NO})^{++}$, brown color
	NO_3^- : to original sample add $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)$ and $\text{AgC}_2\text{H}_3\text{O}_2$ and Na_2CO_3 ; centf., add FeSO_4 and conc. $\text{H}_2\text{SO}_4 \rightarrow \text{Fe}(\text{NO})^{++}$, brown ring

PROCEDURE FOR THE ANALYSIS OF GROUP V

The accumulation of salts of calcium, barium, zinc and silver, added in the form of nitrates as group reagents, will interfere with the tests for the anions of this group and must be removed. To do this, take the solution remaining from the removal of group IV, add solid Na_2CO_3 until alkaline toward litmus, heat to boiling, evaporate in a crucible to a small volume, centrifuge, wash, and use the supernatant liquid for the following tests.

Detection of Chlorate. This test depends upon the reduction of the chlorate to chloride. Conduct the test as follows: To a portion of the afore-mentioned solution, add dilute H_2SO_4 until slightly acid and then a few pieces of solid sodium nitrite, in order to reduce the chlorate to chloride, and heat to boiling. To the boiled solution, add 2 drops of concentrated HNO_3 and 2 drops of AgNO_3 . If a white precipitate (of AgCl) forms, chlorates were present in the original sample.

Detection of Acetate. To a portion of the group V solution in a crucible, add several drops of ethyl alcohol and then enough concentrated H_2SO_4 to double the volume. Heat carefully. Cautiously note the odor of the warm solution. The fruity odor of ethyl acetate, which must not be confused with the odor of alcohol, shows the presence of acetates.

Detection of Nitrite. On the spot plate place a few drops of the solution, and add a crystal of ferrous sulfate and 2 drops of acetic acid. A brown color shows the presence of nitrites.

Detection of Nitrate. Place $\frac{1}{2}$ ml. of the original sample in each of 2 centrifuge tubes. Precipitate all the insoluble barium salts by the addition of barium acetate solution to both tubes. When precipitation seems to be complete, add enough saturated silver acetate solution to precipitate all of the insoluble silver salts. Pour the contents of both tubes into a crucible, and heat the mixture to boiling. Now add a slight excess of solid Na_2CO_3 , which will remove the excess Ag^+ and Ba^{++} ion added in the beginning of the procedure. Heat the mixture to just below boiling, and return the contents of the crucible to the centrifuge tubes. Centrifuge, and discard the precipitate.

Pour the supernatant liquid into the crucible, and add a heaping spatulaful of NH_4Cl ; now add dilute H_2SO_4 , dropwise, until all effervescence ceases, and then add a few drops in excess. Concentrate the solution to 3 or 4 ml. by heating.

The solution is now ready for the ring test: To a portion of this solution, add a few crystals of $FeSO_4$, warming to dissolve them if necessary. Cool under the water tap, and then add, dropwise, concentrated H_2SO_4 , again cooling the tube. A brown ring forming at the junction of the two liquids shows the presence of nitrates in the sample.

ELECTROCHEMICAL THEORY OF OXIDATION-REDUCTION

We are already familiar with the general concept and the electrical nature of the phenomena of oxidation and reduction. Many of the reactions utilized in the procedures of analysis are *redox* reactions and are of several different types, such as (1) the replacement of one metal by another, as in the reduction of Sb^{+++} ion by metallic Zn and Al, or the reduction of the ions of tin by Mg, Fe and Zn; (2) the displacement of a halogen, for example, the oxidation of I^- ion and Br^- ion by Cl_2 ; (3) many cases where the ionic

TABLE XXXV
REACTIONS OF ANIONS

Anion	$\text{Ca}(\text{NO}_3)_2$	$\text{Ba}(\text{NO}_3)_2$	$\text{Zn}(\text{NO}_3)_2$	AgNO_3 (Neutral)	Dilute HCl in Test Solution	Concentrated H_2SO_4
$\text{CO}_3^{=}$	CaCO_3 white	BaCO_3 white	ZnCO_3 white	Ag_2CO_3 white changing to Ag_2O	CO_2	CO_2
$\text{C}_2\text{O}_4^{=}$	CaC_2O_4 white	BaC_2O_4 white		$\text{Ag}_2\text{C}_2\text{O}_4$ white		$\text{CO} + \text{CO}_2$
F^-	CaF_2 white	BaF_2 white	ZnF_2 white			HF
BO_2^-	$\text{Ca}(\text{BO}_2)_2$ white	$\text{Ba}(\text{BO}_2)_2$ white		AgBO_2 white		H_3BO_3
$\text{SO}_3^{=}$	CaSO_3 white	BaSO_3 white	ZnSO_3 white	Ag_2SO_3 white	SO_2	SO_2
AsO_2^-	$\text{Ca}(\text{AsO}_2)_2$ white	$\text{Ba}(\text{AsO}_2)_2$ white		Ag_3AsO_3 yellow		
$\text{AsO}_4^{=}$	$\text{Ca}_3(\text{AsO}_4)_2$ white	$\text{Ba}_3(\text{AsO}_4)_2$ white	$\text{Ba}_3(\text{AsO}_4)_2$ white	Ag_3AsO_4 chocolate		
$\text{PO}_4^{=}$	$\text{Ca}_3(\text{PO}_4)_2$ white	$\text{Ba}_3(\text{PO}_4)_2$ white	$\text{Zn}_3(\text{PO}_4)_2$ white	Ag_3PO_4 yellow		
$\text{C}_4\text{H}_6\text{O}_6^{=}$	$\text{CaC}_4\text{H}_6\text{O}_6$ white		$\text{BaC}_4\text{H}_6\text{O}_6$ white	$\text{Ag}_2\text{C}_4\text{H}_6\text{O}_6$ white		SO_2, CO_2 charring
$\text{SO}_4^{=}$			BaSO_4 white	Ag_2SO_4 white		
$\text{CrO}_4^{=}$			BaCrO_4 yellow	Ag_2CrO_4 red		

S^-	ZnS white	Ag_2S black	H ₂ S	H ₂ S + SO ₂
CN ⁻	Zn(CN) ₂ white	AgCN white	HCN	CO
Fe(CN) ₆ ³⁻	Zn ₃ K ₂ [Fe(CN) ₆] ₂	Ag ₄ Fe(CN) ₆ white		CO
Fe(CN) ₆ ⁴⁻	Zn ₄ [Fe(CN) ₆] ₂ yellow	Ag ₂ Fe(CN) ₆ orange-red		CO
S ₂ O ₈ ²⁻		Ag ₂ S ₂ O ₃ white \rightarrow Ag ₂ S black	SO ₂ + S	SO ₂
CNS ⁻		AgCNS white		
I ⁻		AgI yellow		
Br ⁻		AgBr pale yellow		
Cl ⁻		AgCl white		
ClO ₃ ⁻				
C ₂ H ₃ O ₂ ⁻			AgNO ₂ (in concentrated solution)	NO ₂
NO ₃ ⁻				
SiO ₃ ²⁻	CaSiO ₃ white		Ag ₂ SiO ₃ yellow	

forms of two elements were changed, one ion being oxidized simultaneously while another ion was being reduced to a lower ionic form.

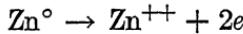
The most important questions which now arise are:

1. What constitutes a measure of the relative oxidizing or reducing ability of a substance?
2. How is such relative strength measured?
3. What is meant by oxidation potential, and how are electrode potentials measured?
4. How are equilibrium constants of *redox* reactions calculated and interpreted?

Answers to the questions are found in the application of the Nernst equation, the fundamental relation between the electric potential of an electrode and the concentration of ions in contact with the electrode.

THE NERNST EQUATION

The dissolving of a metal, that is, passing from the solid (atomic) state to the ionic condition, is a simple case of oxidation, as, for instance, in the case of zinc:



the action being accompanied by the loss of 2 electrons for each ion formed. Conversely, when the ion of a metal gains electrons and is deposited in the metallic condition, the process is one of reduction, as in the case of the deposition of copper:



The formation of zinc ions, when a strip of zinc is placed in water or in a dilute solution of a zinc salt, will leave the strip negatively charged with respect to the solution. Thus there is set up a difference of electric potential at the surface of contact of the metal and its solution. According to Nernst, the value of the potential difference depends, among other factors, on the "solution pressure" of the metal tending to drive atoms into solution and on the osmotic pressure of the ions acting in the opposite direction to force ions out of solution. A mathematical treatment of this concept led Nernst to the following equation for the potential difference, E , between the metal and the solution when equilibrium is attained:

$$E = \frac{RT}{nF} \ln \frac{C}{k}$$

In this equation R is the perfect-gas constant (the value of which is usually given as 1.99 or 2 calories per degree—here, however, it has the equivalent value of 8.315 joules per degree), T is the absolute temperature, n is the number of electrons lost per atom, F is the total amount of charge measured in coulombs on one gram equivalent weight of the ion (1 faraday = 96,494 coulombs), \ln is the symbol for the natural logarithm (to the base $e = 2.71828 \dots$), C is the concentration of the ions in the solution, and k is the so-called Nernst constant which depends upon the solution pressure. If the values of R and F are inserted, taking $T = 298^\circ$, and, if the natural logarithm is changed to the common logarithm (to the base 10) by multiplying by 2.303, this equation simplifies to

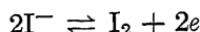
$$E = \frac{0.059}{n} \log \frac{C}{k}$$

The value of C can be found by quantitative analysis, but k cannot be evaluated; hence, there is no direct way in which the value of E can be determined. Relative values of E can be obtained by taking the strip of metal with its solution as one half-cell and connecting it to another reference half-cell, which may be either a standard hydrogen or a standard calomel half-cell. A standard or “normal” hydrogen half-cell consists of a small strip of platinum coated with platinum black and joined to a wire encased in a glass tube. The tube is surrounded by another, larger tube through which a stream of hydrogen is passed. This arrangement is placed in a vessel containing acid whose hydrogen-ion concentration (or, more accurately, hydrogen-ion activity) is exactly 1 molal. Such a half-cell is arbitrarily assigned a potential of zero.

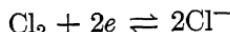
If then a zinc half-cell is joined, by an external circuit containing a voltmeter or potentiometer, to a hydrogen half-cell, and the two solutions are connected by means of a salt bridge, the voltage indicated on the instrument will be the difference between that of the zinc half-cell and that of the hydrogen half-cell. Since the standard hydrogen half-cell potential has been taken as zero, the potential of the zinc half-cell will be the value indicated by the measuring instrument. In this way it has been found that for a zinc half-cell, when the concentration of zinc ions is exactly molal, the potential is -0.7620 volt. Similarly, for a copper half-cell, the molal potential is $+0.3448$ volt. The potential of a half-

cell made up of an element and a molal solution of its ions commonly is referred to as the single-electrode potential of the element. If these single-electrode potentials are arranged in order of magnitude, the result is the familiar electromotive series of the metals.

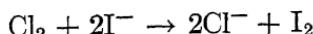
A similar series of electrode potentials is obtained for the non-metallic elements; for example, in the electron equations,



and

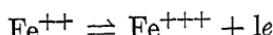


where, when combined into the *redox* reaction,



the iodide ion is oxidized while the chlorine is reduced.

For half-cell or electron reactions of the types,



and



which represent the most numerous of the *redox* reactions, electrode potentials, likewise, have been determined. In fact, the values for a great many electron reactions of various types, when inserted in the series for the metals, constitute an extensive table of electrode potentials. This is simply an extension of the electromotive series to oxidation and reduction reactions, which do not necessarily involve an element in the free form. Extensive tables of this type are available; some representative values are included in Table XXVI. In this table a large negative value indicates a strong reducing tendency of the substance on the left in the half-cell equation; similarly, a large positive value indicates a strong oxidizing tendency of the substance on the left in the equation. It is not correct to say that negative values indicate reducing agents and positive values oxidizing agents; we must specify that negative values *indicate stronger reducing agents than hydrogen*, and positive values analogously.

The most important use of the potential series is to enable us to predict whether a reaction of oxidation-reduction between two substances will take place at all or effectively. The most general conclusion is that the farther apart the substances are in the series, that is, the greater the difference in their electrode potentials, the

TABLE XXVI
STANDARD OXIDATION-REDUCTION POTENTIALS

<i>Oxidizing Potential Referred to Normal Hydrogen Electrode = 0</i>	<i>Electron Reaction</i>
*	$\text{BiO}_3^- + 6\text{H}^+ + 2e \rightleftharpoons \text{Bi}^{+++} + 3\text{H}_2\text{O}$
*	$\text{IO}_4^- + 2\text{H}^+ + 2e \rightleftharpoons \text{IO}_3^- + \text{H}_2\text{O}$
*	$\frac{1}{2}\text{S}_2\text{O}_8^{=+} + e \rightleftharpoons \text{SO}_4^{=}$
1.82	$\text{Co}^{+++} + e \rightleftharpoons \text{Co}^{++}$
1.78	$\frac{1}{2}\text{H}_2\text{O}_2 + \text{H}^+ + e \rightleftharpoons \text{H}_2\text{O}$ (action toward reducing agents)
1.68	$\text{PbO}_2 + 4\text{H}^+ + \text{SO}_4^{=+} + 2e \rightleftharpoons \text{PbSO}_4 + 2\text{H}_2\text{O}$
1.59	$\text{MnO}_4^- + 4\text{H}^+ + 3e \rightleftharpoons \text{MnO}_2 + 2\text{H}_2\text{O}$
1.5	$\text{MnO}_4^- + 8\text{H}^+ + 5e \rightleftharpoons \text{Mn}^{++} + 4\text{H}_2\text{O}$
1.49	$\text{BrO}_3^- + 6\text{H}^+ + 5e \rightleftharpoons \frac{1}{2}\text{Br}_2 + 3\text{H}_2\text{O}$
1.45	$\text{Ce}^{++++} + e \rightleftharpoons \text{Ce}^{+++}$
1.45	$\text{ClO}_3^- + 6\text{H}^+ + 6e \rightleftharpoons \text{Cl}^- + 3\text{H}_2\text{O}$
1.42	$\text{BrO}_3^- + 6\text{H}^+ + 6e \rightleftharpoons \text{Br}^- + 3\text{H}_2\text{O}$
1.36	$\text{Au}^{+++} + 3e \rightleftharpoons \text{Au}$
1.36	$\frac{1}{2}\text{Cl}_2 + e \rightleftharpoons \text{Cl}^-$
1.35	$\text{ClO}_4^- + 8\text{H}^+ + 8e \rightleftharpoons \text{Cl}^- + 4\text{H}_2\text{O}$
1.33	$\text{MnO}_2 + 4\text{H}^+ + 2e \rightleftharpoons \text{Mn}^{++} + 2\text{H}_2\text{O}$
1.3	$\frac{1}{2}\text{Cr}_2\text{O}_7^{=+} + 7\text{H}^+ + 3e \rightleftharpoons \text{Cr}^{+++} + \frac{7}{2}\text{H}_2\text{O}$
1.23	$\frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2e \rightleftharpoons \text{H}_2\text{O}$ (in acid solution)
1.21	$\text{Ti}^{+++} + 2e \rightleftharpoons \text{Ti}^+$
1.20	$\text{IO}_3^- + 6\text{H}^+ + 5e \rightleftharpoons \frac{1}{2}\text{I}_2 + 3\text{H}_2\text{O}$
1.09	$\text{IO}_3^- + 6\text{H}^+ + 6e \rightleftharpoons \text{I}^- + 3\text{H}_2\text{O}$
1.06	$\frac{1}{2}\text{Br}_2 + e \rightleftharpoons \text{Br}^-$
0.94	$\text{NO}_3^- + 4\text{H}^+ + 3e \rightleftharpoons \text{NO} + 2\text{H}_2\text{O}$
0.92	$\text{VO}_3^- + \text{H}_2\text{SO}_4 + 2\text{H}^+ + e \rightleftharpoons \text{VOSO}_4 + 2\text{H}_2\text{O}$
0.90	$\text{Hg}^{++} + e \rightleftharpoons \frac{1}{2}\text{Hg}_2^{++}$
0.86	$\text{Hg}^{++} + 2e \rightleftharpoons \text{Hg}$
0.80	$\frac{1}{2}\text{Hg}_2^{++} + e \rightleftharpoons \text{Hg}$
0.80	$\text{Ag}^+ + e \rightleftharpoons \text{Ag}$
0.78	$\text{Fe}^{+++} + e \rightleftharpoons \text{Fe}^{++}$
0.75	$\text{SbO}_4^{=+} + 2\text{H}^+ + 2e \rightleftharpoons \text{SbO}_3^{=+} + \text{H}_2\text{O}$
0.74	$\text{H}_2\text{SeO}_3 + 4\text{H}^+ + 4e \rightleftharpoons \text{Se} + 3\text{H}_2\text{O}$
0.68	$\frac{1}{2}\text{O}_2 + \text{H}^+ + e \rightleftharpoons \frac{1}{2}\text{H}_2\text{O}_2$ (reducing action toward stronger oxidants)
0.66	$\text{MnO}_4^- + e \rightleftharpoons \text{MnO}_4^{=}$
0.59	$\text{MnO}_4^- + 2\text{H}_2\text{O} + 3e \rightleftharpoons \text{MnO}_2 + 4\text{OH}^-$
0.57	$\text{AsO}_4^{=+} + 2\text{H}^+ + 2e \rightleftharpoons \text{AsO}_3^{=+} + \text{H}_2\text{O}$
0.53	$\frac{1}{2}\text{I}_2 + e \rightleftharpoons \text{I}^-$
0.5	$\text{MoO}_3 + 4\text{H}^+ + e \rightleftharpoons \text{MoO}^{+++} + 2\text{H}_2\text{O}$
0.49	$\text{Fe}(\text{CN})_6^{=+} + e \rightleftharpoons \text{Fe}(\text{CN})_6^{=+}$
0.47	$\text{H}_2\text{SO}_3 + 4\text{H}^+ + 4e \rightleftharpoons \text{S} + 3\text{H}_2\text{O}$
* 0.4	$\text{VO}_3^- + 6\text{H}^+ + 3e \rightleftharpoons \text{V}^{++} + 3\text{H}_2\text{O}$
0.4	$\text{VO}^{++} + 2\text{H}^+ + e \rightleftharpoons \text{V}^{++} + \text{H}_2\text{O}$
* 0.4	$\text{PtCl}_6^{=+} + 2e \rightleftharpoons \text{PtCl}_4^{=+} + 2\text{Cl}^-$

* Approximate value or position.

TABLE XXVI (*Continued*)

STANDARD OXIDATION-REDUCTION POTENTIALS

*Oxidizing Potential**Referred to Normal**Hydrogen Electrode = 0**Electron Reaction*

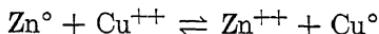
0.40	$\frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2e \rightleftharpoons 2\text{OH}^-$
0.36	$\text{UO}_2\text{SO}_4 + 4\text{H}^+ + \text{SO}_4^- + 2e \rightleftharpoons \text{U}(\text{SO}_4)_2 + 2\text{H}_2\text{O}$
0.34	$\text{Cu}^{++} + 2e \rightleftharpoons \text{Cu}$
0.333	Decinormal calomel electrode
* 0.3	$\text{WO}_3 + 4\text{H}^+ + e \rightleftharpoons \text{WO}^{+++} + 2\text{H}_2\text{O}$
0.280	Normal calomel electrode
0.23	$\text{AgCl} + e \rightleftharpoons \text{Ag} + \text{Cl}^-$
0.2	$\text{PtCl}_4^- + 2e \rightleftharpoons \text{Pt} + 4\text{Cl}^-$
0.2	$\text{Bi}^{+++} + 3e \rightleftharpoons \text{Bi}$
0.17	$\text{S} + 2\text{H}^+ + 2e \rightleftharpoons \text{H}_2\text{S}$
0.17	$\text{Cu}^{++} + e \rightleftharpoons \text{Cu}^+$
0.15	$\text{Sn}^{++++} + 2e \rightleftharpoons \text{Sn}^{++}$
0.14	$\text{SO}_4^- + 4\text{H}^+ + 2e \rightleftharpoons \text{H}_2\text{SO}_3 + \text{H}_2\text{O}$
* 0.1	$\text{WO}^{+++} + 2\text{H}^+ + e \rightleftharpoons \text{W}^{++++} + \text{H}_2\text{O}$
0.04	$\text{TiO}^{++} + 2\text{H}^+ + e \rightleftharpoons \text{Ti}^{+++} + \text{H}_2\text{O}$
* 0.0	$\text{MoO}_3 + 6\text{H}^+ + 3e \rightleftharpoons \text{Mo}^{+++} + 3\text{H}_2\text{O}$
0.000	$\text{H}^+ + e \rightleftharpoons \frac{1}{2}\text{H}_2$
-0.12	$\text{Pb}^{++} + 2e \rightleftharpoons \text{Pb}$
-0.14	$\text{Sn}^{++} + 2e \rightleftharpoons \text{Sn}$
* -0.2	$\text{CO}_2 + \text{H}^+ + e \rightleftharpoons \frac{1}{2}\text{H}_2\text{C}_2\text{O}_4$
-0.2	$\text{V}^{+++} + e \rightleftharpoons \text{V}^{++}$
-0.23	$\text{Ni}^{++} + 2e \rightleftharpoons \text{Ni}$
-0.29	$\text{Co}^{++} + 2e \rightleftharpoons \text{Co}$
-0.34	$\text{Tl}^+ + e \rightleftharpoons \text{Tl}$
-0.38	$\text{In}^{+++} + 3e \rightleftharpoons \text{In}$
-0.40	$\text{Cd}^{++} + 2e \rightleftharpoons \text{Cd}$
-0.40	$\text{Cr}^{+++} + e \rightleftharpoons \text{Cr}^{++}$
-0.44	$\text{Fe}^{++} + 2e \rightleftharpoons \text{Fe}$
-0.5	$\text{Ga}^{+++} + 3e \rightleftharpoons \text{Ga}$
-0.56	$\text{Cr}^{++} + 2e \rightleftharpoons \text{Cr}$
-0.76	$\text{Zn}^{++} + 2e \rightleftharpoons \text{Zn}$
-1.1	$\text{Mn}^{++} + 2e \rightleftharpoons \text{Mn}$
-1.4	$\text{U}^{++++} + 4e \rightleftharpoons \text{U}$
-1.69	$\text{Be}^{++} + 2e \rightleftharpoons \text{Be}$
-1.7	$\text{Al}^{+++} + 3e \rightleftharpoons \text{Al}$
-2.40	$\text{Mg}^{++} + 2e \rightleftharpoons \text{Mg}$
-2.71	$\text{Na}^+ + e \rightleftharpoons \text{Na}$
-2.76	$\text{Ca}^{++} + 2e \rightleftharpoons \text{Ca}$
-2.90	$\text{Ba}^{++} + 2e \rightleftharpoons \text{Ba}$
-2.92	$\text{Sr}^{++} + 2e \rightleftharpoons \text{Sr}$
-2.92	$\text{K}^+ + e \rightleftharpoons \text{K}$
-2.93	$\text{Rb}^+ + e \rightleftharpoons \text{Rb}$
-2.96	$\text{Li}^+ + e \rightleftharpoons \text{Li}$

* Approximate value or position.

more likelihood is there of a vigorous, pronounced and more complete reaction. For example Zn will replace Cu⁺⁺ ion from solution more readily than will metallic Fe, and Cl₂ will replace iodides from solution more readily than will Br₂. Likewise, the MnO₄⁻ ion is a stronger oxidizing agent toward, for example, Fe⁺⁺ ion than is the Cr₂O₇⁼ ion.

Equilibrium Constants of Redox Reactions. Redox reactions, like all others, are reversible and reach a state of equilibrium. They therefore are characterized by equilibrium constants which can be calculated. Some illustrations are given here.

Calculation of Equilibrium Constants. In the replacement of copper by zinc the reaction is



If we apply the Law of Chemical Equilibrium to this reaction, the equilibrium equation becomes

$$\frac{C_{\text{Zn}^{++}} \times C_{\text{Cu}^\circ}}{C_{\text{Cu}^{++}} \times C_{\text{Zn}^\circ}} = k$$

and equilibrium is reached when the value of k is satisfied. Since the factors C_{Cu° and C_{Zn° represent the solid metallic condition, they may be considered constant quantities, and the foregoing equation becomes simply:

$$\frac{C_{\text{Zn}^{++}}}{C_{\text{Cu}^{++}}} = K \quad (\text{equilibrium constant})$$

This means that, when the concentration of zinc ions bears a certain ratio to that of the copper ions, the reaction will have reached equilibrium. The equilibrium ratio, that is, the equilibrium constant, K , for this reaction is calculated from electrochemical data using electrode potentials and applying the Nernst equation.

If a zinc-zinc salt solution half-cell and a copper-copper salt solution half-cell are joined externally through an ammeter and internally by a salt bridge, a stream of electrons will flow from the zinc electrode through the ammeter to the copper electrode. In this process zinc will go into solution, making the zinc solution more concentrated, and copper will be plated out, making the copper solution less concentrated. The current will cease when the system has come to equilibrium. This will occur when the electrode potential of the zinc equals that of the copper, which will

be realized when the ratio of the concentration of zinc ion to that of copper ion has attained a definite value, as previously stated. This ratio can be calculated in the following way:

The Nernst equation,

$$E = \frac{0.059}{n} \log \frac{C}{k}$$

may be rewritten in the form:

$$E = \frac{0.059}{n} \log \frac{1}{k} + \frac{0.059}{n} \log C$$

When the concentration is molal, $C = 1$, $\log C = 0$, and the molal potential E_0 is given by $\frac{0.059}{n} \log \frac{1}{k}$. From this the potential of the electrode for any concentration may be expressed by the equation:

$$E = E_0 + \frac{0.059}{n} \log C$$

For the zinc electrode,

$$E_{(\text{zinc})} = E_{0(\text{zinc})} + \frac{0.059}{2} \log C_{\text{Zn}^{++}}$$

and for the copper electrode,

$$E_{(\text{copper})} = E_{0(\text{copper})} + \frac{0.059}{2} \log C_{\text{Cu}^{++}}$$

At equilibrium, when $E_{(\text{zinc})}$ is equal to $E_{(\text{copper})}$,

$$E_{0(\text{zinc})} + \frac{0.059}{2} \log C_{\text{Zn}^{++}} = E_{0(\text{copper})} + \frac{0.059}{2} \log C_{\text{Cu}^{++}}$$

If we insert values from Table XXVI,

$$-0.76 + 0.0295 \log C_{\text{Zn}^{++}} = 0.34 + 0.0295 \log C_{\text{Cu}^{++}}$$

collect terms,

$$1.10 = 0.0295 (\log C_{\text{Zn}^{++}} - \log C_{\text{Cu}^{++}})$$

and rewrite,

$$\log \frac{C_{\text{Zn}^{++}}}{C_{\text{Cu}^{++}}} = \frac{1.10}{0.0295} = 37.3$$

$$\frac{C_{\text{Zn}^{++}}}{C_{\text{Cu}^{++}}} = 1 \times 10^{37.3} = 2 \times 10^{37}$$

$$\therefore K = 2 \times 10^{37}$$

That is, K , the ratio of the Zn^{++} concentration to the Cu^{++} concentration, is 2×10^{37} . This means that, when equilibrium is reached in the reaction in which zinc displaces copper ions, the concentration of Zn^{++} is enormous, and the concentration of Cu^{++} remaining in solution is negligible; for practical purposes the removal of copper ions is complete.

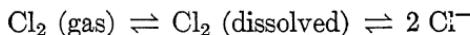
When an electronegative element, such as sulfur or chlorine, dissolves, negatively charged ions (anions) are formed, and the process is one of reduction. For chlorine, for example, the reaction is



For an element of this type the electrode is positive with respect to the solution, and so the sign of the half-cell potential must be reversed:

$$E = -\frac{0.059}{n} \log \frac{C_{\text{anion}}}{k}$$

A half-cell containing a chlorine electrode has equilibria of the type



established. Consequently, C_{anion} depends upon the amount of Cl_2 in solution; that is, it depends upon the solubility of the gas. Since from the foregoing equation,

$$\frac{(C_{Cl^-})^2}{C_{Cl_2(\text{dissolved})}} = \kappa$$

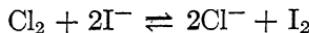
we may substitute for C_{anion} the ratio given by κ in order to take account of the effect of the solubility of the gas on the half-cell potential. This gives

$$\begin{aligned} E &= \frac{-0.059}{2} \log \frac{(C_{Cl^-})^2}{C_{Cl_2}} \times \frac{1}{k} = \frac{0.059}{2} \log \frac{C_{Cl_2} \times k}{(C_{Cl^-})^2} \\ &= \frac{0.059}{2} \left(\log \frac{C_{Cl_2}}{(C_{Cl^-})^2} + \log k \right) \end{aligned}$$

The molal electrode potential is then given by

$$E_{(Cl)} = E_{0(Cl)} + \frac{0.059}{2} \log \frac{C_{Cl_2}}{(C_{Cl^-})^2}$$

E_0 for chlorine has been found to be +1.3583 volts. The corresponding value of E_0 for iodine is +0.5345. The values show chlorine to be a stronger oxidizing agent than iodine and the iodide ion a stronger reducing agent than the chloride ion. Chlorine therefore will oxidize iodides, in accordance with the equation:



The equilibrium constant of this reaction is expressed by the equation:

$$\frac{(C_{\text{Cl}^-})^2 \times C_{\text{I}_2}}{(C_{\text{I}^-})^2 \times C_{\text{Cl}_2}} = K$$

By applying the same method as was used in determining the $C_{\text{Zn}^{++}} - C_{\text{Cu}^{++}}$ ratio, we can determine the corresponding value for the displacement of iodine by chlorine. We have then

$$E_{0(\text{Cl})} + \frac{0.059}{2} \log \frac{C_{\text{Cl}_2}}{(C_{\text{Cl}^-})^2} = E_{0(\text{I})} + \frac{0.059}{2} \log \frac{C_{\text{I}_2}}{(C_{\text{I}^-})^2}$$

Transforming, we have

$$\frac{0.059}{2} \left(\log \frac{C_{\text{I}_2}}{(C_{\text{I}^-})^2} - \log \frac{C_{\text{Cl}_2}}{(C_{\text{Cl}^-})^2} \right) = 1.3583 - 0.5345$$

and rewriting,

$$\log \frac{(C_{\text{Cl}^-})^2 \times C_{\text{I}_2}}{(C_{\text{I}^-})^2 \times C_{\text{Cl}_2}} = \frac{0.8238}{0.0295}$$

$$\log K = 27.90$$

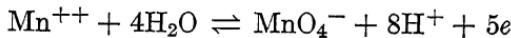
$$K = 1 \times 10^{27.90} = 7.9 \times 10^{27}$$

The value of K shows that the reaction runs very far toward completion.

With elements which exist in two different ionic forms, such as, for example, the reversible change for the oxidation of ferrous ions and reduction of ferric ions,

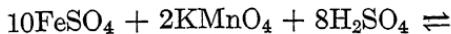


and with the more complex relationships, as in the oxidation of manganous ion and reduction of the MnO_4^- ion in acid solution,

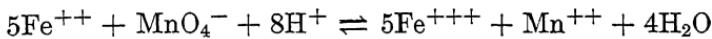


the molal potentials can be determined and the ions arranged in similar series. Some of these for which data exist are given in Table XXVI.

Equilibrium constants for any interaction between an oxidizing substance and a reducing substance can be calculated from electrochemical data. For the reaction,



rewritten in ionic form,



the equilibrium constant is expressed by

$$\frac{(C_{\text{Fe}^{+++}})^5 \times C_{\text{Mn}^{++}}}{(C_{\text{Fe}^{++}})^5 \times C_{\text{MnO}_4^-} \times (C_{\text{H}^+})^8} = K$$

By combining the potentials for the $\text{Fe}^{++}-\text{Fe}^{+++}$ and $\text{Mn}^{++}-\text{MnO}_4^-$ half-cells, the value of the constant can be found. In this way one can calculate whether any particular oxidation-reduction reaction will take place, and, if it does, how near to completion it will go before equilibrium is attained.

QUESTIONS AND PROBLEMS—SET 10

1. What is a half-cell? A salt bridge? Describe a standard hydrogen electrode.
2. Calculate the equilibrium constant for the displacement of Ag by Pb.
3. Will metallic iron reduce stannic ions to the stannous condition? Answer by reference to Table XXVI.
4. Magnesium is above aluminum in the table. Why does aluminum not plate out when a strip of magnesium is placed in a solution of an aluminum compound?
5. What potential would be developed at 25° by a cell consisting of a molal Mg half-cell and a molal Pb half-cell?
6. Apply Nernst's equation to two half-cells, made up of the same electrode material and containing the same electrolyte, but at two different concentrations. Combine the two equations, and thus obtain the expression for the potential of a concentration cell.
7. Apply the answer to question 6 to two Zn-ZnSO₄ half-cells, one containing 1 molal ZnSO₄ and the other 0.1 molal ZnSO₄. What is the potential of the combination? What is the electrode reaction in each half-cell? When will equilibrium be attained?

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8. If you wish to prepare Cl_2 by oxidizing HCl , is KMnO_4 or $\text{K}_2\text{Cr}_2\text{O}_7$ the better oxidizing agent? Answer by reference to Table XXVI.
9. Why is Cl_2 liberated instead of O_2 when a solution of NaCl is electrolyzed?
10. Suppose that you had a solution containing Au^{+++} , Ag^+ , Cu^{++} and Cd^{++} . How would you proceed to separate them electrolytically?
11. Find the equilibrium constant for the reaction between I^- and Br_2 .
12. If you wished to use H_2S as a reducing agent, would it be more effective to have the solution acid or basic?

PART III. SYSTEMATIC ANALYSIS

CHAPTER IX

A complete qualitative chemical analysis of a sample of material consists of the separate systematic detection of cations and anions. The results will show not only which cations and anions are present but which are absent as well. Within the scope of this book, provision has been made for the study and detection of the ions of 32 of the commoner elements. In the case of a homogeneous substance, such as a single salt, the positive detection of a single cation and of a single anion usually will identify the salt present. On the other hand, in a sample of greater complexity, such as a mixture of salts, a qualitative analysis usually can discover only which cations and anions are present and not how they may have been associated with each other in the original mixture.

A complete systematic analysis involves

- A. The preliminary examination and preparation of the sample.
- B. The detection of anions.
- C. The detection of cations.
- D. The examination of the acid-insoluble residue.

Since most of the anions interfere in one way or another with the cation analysis, it is advisable to complete the anion analysis before the cation detection is begun.

Types of Samples. In order to simplify the work and to keep the procedures from becoming too involved for the beginning student, the work outlined in this book provides for the analysis of samples of several different types, as follows:

1. Liquid samples, hereafter referred to as "test solution unknowns," composed of mixtures of cations of several or all cation groups and of mixtures of anions of several or all anion groups. This kind of student sample is referred to again on page 320.
2. Solids consisting of a single compound. See page 321.

3. Solid mixtures of salts. This type of sample consists of unknowns made up of solid mixtures of two or more common salts (see page 323).

4. Alloys and metals. Samples of this kind involve the detection of cations and of a limited number of anions (see page 329).

A. PRELIMINARY EXAMINATION AND PREPARATION OF THE SAMPLE

1. SYSTEMATIC ANALYSIS OF "TEST SOLUTION UNKNOWNs"

These are the samples, submitted earlier in the laboratory work, which consist of mixtures of cations or of anions of all groups or at least combinations of several groups. They are prepared by mixing quantities of the "10-milligram" or stock test solutions. The components usually are already in solution; hence no special provision need be made for dissolving the sample. Since the cation samples are derived mainly from the nitrates of the metals and the anion samples from the sodium or potassium salts, interferences normally are not encountered with this type of sample.

The procedures of analysis, already developed in Parts I and II, are incorporated in the condensed "blocked-out" schemes which follow, that for anion detection beginning on page 330, and that for cation detection beginning on page 337. The cation sample designated "general cation sample" is to be analyzed for members of all groups unless otherwise instructed and will be issued at the conclusion of the laboratory work of Part I on individual cation groups. The "general anion sample" will be submitted when the laboratory work on individual anion groups has been finished.

The Cation Sample. This should contain from 2 to 5 milligrams per milliliter of each cation present. The sample will be free from interfering anions, oxidizing agents and large amounts of strong acids. If a precipitate is present, indicating either oxysalts of bismuth or antimony, or else precipitated chlorides of group I, shake the container well, so that a proportionate part of the solid will be included in the portion taken for analysis. A colored solution will indicate the presence of copper, ferric iron, chromium, nickel or cobalt.

Test a drop of the sample with dilute $KMnO_4$ acidified with dilute H_2SO_4 for the presence of reducing cations, and correlate this observation with the results obtained in the systematic procedure.

Take 1 ml. of the well-shaken sample, and proceed with the identification of the cations, turning to page 337 for the scheme of analysis.

The Anion Sample. This sample should contain at least 5 milligrams per milliliter of each anion present. Since the sample is compounded from the (stock) anion test solutions, the only cations which could be present are sodium and potassium, and hence no interference will result. A colored solution will be due to chromates, ferrocyanides or ferricyanides. Test a drop of the sample for the presence of reducing anions by acidifying it and adding a drop of dilute KMnO_4 .

Take a 1-ml. portion of the well-shaken sample, and proceed with the identification of the anions, turning to page 330 for the scheme of analysis.

2. SYSTEMATIC IDENTIFICATION OF A SINGLE SOLID COMPOUND

Samples composed of a single substance, usually a solid, generally are submitted for student analysis after the separate procedures for cation and anion analysis have been studied and "test solution unknowns" have been analyzed, but before the analyses of more complicated samples, such as solid mixtures of salts, alloys, or other materials, are undertaken. The sample may be a simple salt, an acid, an alkali or an oxide. In general, the procedure for the identification of the substance consists of a systematic search for the anion, followed by that for the cation. A definite pronounced test for an anion, as well as that for a cation, will identify the compound as a salt. If, however, an anion is definitely detected and no metallic ion can be found, the conclusion is that the sample is an acid, the cation being the hydrogen ion. On the other hand, if a cation is found, but no anion, the substance is either a hydroxide or an oxide.

A preliminary examination of the sample is first made. This is followed by the preparation of the anion solution, which is employed for the anion analysis. After this, the cation solution is prepared and used for the detection of cations. Before the identity of the compound is reported, the solubility table (page 376) should be consulted, and conclusions correlated with other observations, so that the report will be consistent with these observations.

Preliminary Examination. Note the color; if not white or colorless, the substance may be a compound of silver, mercury, lead, copper, iron, chromium, manganese, nickel or cobalt.

Determine whether the substance is water-soluble. If so, test a drop with acidified KMnO_4 reagent for the presence of reducing ions. Test another drop of the water solution with litmus paper; this will reveal the presence of a free acid, a free base or a salt which has hydrolyzed.

Add a drop of HCl to a bit of the sample, and note whether a gas is evolved.

Preparation of the Anion Solution. Whether or not the sample is water-soluble, take about 0.05 gram of the solid, add 1 ml. of 1 *M* Na_2CO_3 , and boil for 5 minutes. This treatment will transpose the anion into the soluble sodium salt and, at the same time, precipitate and remove the cation as an insoluble carbonate, basic carbonate or hydroxide. Dilute the solution to 2 ml., centrifuge, and use the centrifugate for the anion analysis, beginning on page 330. This solution is referred to as the "Prepared Anion Solution."

When the anion present has been identified, another portion of the sample is dissolved in water or acids as described on page 328, and this solution is used for the detection of the cations, as described later, page 337.

Before the cation solution is made and the analysis is begun, the solubility relationships should be considered, so that, since now the anion is known, some clues can be discovered regarding the cation likely to be present. For this purpose the solubility table (see pages 376 and 377) should be consulted. For example, suppose the sample is found to be a carbonate and is water-soluble; obviously, since the table shows all normal carbonates to be insoluble in water except Na_2CO_3 and K_2CO_3 (and $(\text{NH}_4)_2\text{CO}_3$), the sample must be an alkali carbonate. Or, again, suppose the sample is a water-insoluble sulfate; this fact limits the cation to lead or the alkaline earth elements. In this way, much help can be derived from the solubility table. The color of the compound also should be taken into consideration at this time.

There is likely to be no serious interference of anions with the cation procedure with these simple substances, and no special procedure except for phosphates, oxalates or tartrates need be introduced.

Preparation of the Cation Solution. The procedure for dissolving the sample depends upon its solubility.

1. If the sample is rather soluble in water, take a 0.05-gram portion, add 2 ml. of distilled water, and heat to boiling. This will furnish a sufficient amount of the cation for its detection. Turn to the cation scheme on page 337 and follow the procedure until a decisive test is obtained.

2. If the sample is not appreciably soluble in water, treat a 0.05-gram portion of the sample with 2 ml. of dilute HNO_3 , warm the mixture, and add more acid as long as action continues. If the sample completely dissolves, evaporate the solution almost to dryness, dilute with 2 ml. of dilute HNO_3 and enough water to bring the volume to 3 ml., and proceed with the cation detection on page 337. If dilute HNO_3 fails to dissolve the sample completely, add 1 ml. of concentrated HNO_3 to the dilute HNO_3 used as original solvent, heat, and, if no residue remains, evaporate, and dilute as before.

3. If dilute or concentrated HNO_3 fails to dissolve the sample, repeat the procedure, using dilute HCl , and, if this fails, use aqua regia; in either case evaporating to small bulk in the presence of HNO_3 , diluting to 3 ml., and using the resulting solution for the cation detection, as described on page 337.

4. If all solvents fail to dissolve the sample, it must be examined according to the procedure for "Acid-Insoluble Residues" (see page 346).

3. SYSTEMATIC ANALYSIS OF MIXTURES OF SOLID SALTS

Preliminary Examination of Sample. A preliminary physical examination of the sample may throw considerable light on its nature and probable composition. Note the color and physical form. If possible, separate a small portion of the sample into its component salts, and examine the separated compounds for individual characteristics. If a physical separation is possible, special tests on the separated portions may be made later to confirm the results of the systematic analysis.

Treat a small portion of the sample with hot water, and note the color of the resulting solution or supernatant liquid; a colored solution may be due to the presence of water-soluble salts of copper, cobalt, nickel, iron or chromium, or to soluble chromates, dichromates, ferrocyanides or ferricyanides. Test the solution with lit-

mus paper; an alkaline reaction will indicate a free base or salts which have hydrolyzed to give an alkaline solution, such as acetates, carbonates, sulfides, phosphates and borates; an acid reaction will indicate free acid, an acid salt or salts of heavy metals such as FeCl_3 which hydrolyze to give an acidic solution.

Add dilute HCl to another small portion of the sample. If a gas is given off, the possible presence of carbonates, sulfides, sulfites, cyanides, thiosulfates or nitrites will be revealed. Be careful about smelling the gas if cyanides are likely to be present.

Heating a portion of the sample in a hard glass tube is useful in revealing the presence of organic matter, though another test for organic matter is recommended in the procedure.

Blowpipe tests, bead tests and the action of concentrated H_2SO_4 sometimes are resorted to in the preliminary examination, but the results are often hard for the beginner to interpret. The additional information secured is useful, however, in correlating the results of the systematic analysis.

In a complete systematic analysis of samples, especially of the kind under consideration, it is best to carry out the detection of anions before that of the cations. With the exception of a few anions, such as the nitrate, most anions interfere with the regular scheme for the detection of the cations. By identifying the anions first, the proper steps then can be taken to prepare the solution for the cation analysis, introducing modifications in the regular scheme that will remove or otherwise overcome the interferences caused by the presence of these anions. The logical order, therefore, is to find out what anions are present and what interference might result and then proceed later with the preparation of the cation solution and its analysis; provision is made, however, in the systematic cation procedure for the detection of cations in the presence of certain interfering anions independent of a prior complete anion analysis in cases where special emphasis is to be given to the cation content of the sample.

Preparation of the Anion Solution. In the procedure for the detection of anions, the sample must be rendered soluble, and, since most of the cations interfere, they must be removed. Acids cannot be used as solvents, but instead Na_2CO_3 is used.

Take a portion of the thoroughly mixed and powdered solid sample of about 0.05 gram (if balances are not available, the instructor will indicate a suitable amount of sample to use), add to it 1 ml. of 1 M Na_2CO_3 solution, and boil for 5 minutes. Decant

off the supernatant liquid into a beaker, and repeat the Na_2CO_3 treatment. Combine the solutions for the anion analysis (turn to page 330) and reserve the residue for special tests.

This treatment will transpose the anions into soluble sodium salts and precipitate the cations as insoluble carbonates, basic carbonates or hydroxides. A few substances such as silicates, the halides of silver and certain phosphates are not transposed by mere boiling with Na_2CO_3 . If these are suspected and not found by the regular procedure, the sodium carbonate residue should be examined for their presence.

General Considerations of Cation Analysis. With samples consisting of mixtures of solid salts, where interfering anions, strong acids, oxidizing agents and organic matter may be present, special care must be taken in the preparation of the sample for the cation analysis, and consideration must be given to the possibility of interferences. Before suitable means can be provided to correct for these interferences, we should know in what ways these objectionable substances interfere.

In a general way we can say that the difficulties encountered are of three kinds:

1. High concentrations of strong acids, especially the oxidizing acids, HNO_3 and aqua regia, as well as oxidizing agents, such as $\text{K}_2\text{Cr}_2\text{O}_7$, KMnO_4 and FeCl_3 , interfere by reacting with the H_2S used in the precipitation of sulfides and by producing colloidal or free sulfur or insoluble sulfates.

2. Anions of groups I and II, in a neutral or basic solution, will precipitate insoluble salts if Ca^{++} , Ba^{++} , Sr^{++} or Mg^{++} (and possibly Pb^{++}) are present, and this will make detection of these cations uncertain or even impossible unless modifications are introduced.

3. The formation of complex ions with certain anions and cations may prevent the precipitation of the cations in question.

In addition, certain anions interfere with the regulation of the sulfide-ion concentration, produce insoluble compounds, or otherwise obstruct the simple operation of the regular scheme of analysis.

Before the specific interference of the individual anions is discussed, it may be well to state at this point that there is a general method applicable to the removal of many of these troublesome substances. This consists of volatilizing or destroying them by fuming down the solution with H_2SO_4 . The details of this method are described later. In certain cases there is a simpler way out of

the difficulty, but the method nevertheless must be employed for the removal of certain objectionable substances, and, moreover, if for any reason the anion analysis has not yet been made, the treatment with H_2SO_4 must be resorted to.

The chief causes of difficulty, together with a hint for overcoming the interference, are enumerated briefly here, the anions being listed in the order of the systematic anion scheme.

Carbonates. Carbonates do not interfere. They will be evolved as CO_2 during acid treatment in dissolving the sample or during precipitation of group I.

Oxalates. Oxalates cause the premature precipitation of Ca^{++} , Sr^{++} , Ba^{++} and Mg^{++} in group III. They can be removed by the general fuming-down method or by the special method described on page 342.

Fluorides. Fluorides interfere the same as oxalates. They can be removed as HF by fuming down with H_2SO_4 .

Borates. Borates interfere the same as oxalates and are volatilized as boric acid with H_2SO_4 .

Sulfites. Sulfites will react with H_2S to produce free or colloidal sulfur in group II. They can be removed by acid treatment.

Arsenites. There is no interference. Arsenites are precipitated as As_2S_3 in cation group II according to regular procedure.

Arsenates. Arsenates are slowly and possibly incompletely precipitated in cation group II unless reduced with NH_4I according to the regular procedure.

Phosphates. There is serious interference since Ca^{++} , Sr^{++} , Ba^{++} and Mg^{++} will be precipitated as phosphates in group III. In the presence of phosphates, the modification of the procedure described on page 342 must be used.

Tartrates. Tartrates interfere in the same way as oxalates and phosphates. Besides, the tartrate ion forms complexes with Al and Cr and prevents precipitation of these cations. They can be removed by fuming down according to (a) the general method or (b) the method described on page 342.

Sulfates. Sulfates will cause precipitation of $BaSO_4$, $SrSO_4$, $PbSO_4$ and possibly $CaSO_4$. These cations then are sought for in the acid-insoluble residue, according to the procedure given on page 346.

Chromates. Chromates interfere by reducing the hydrogen sulfide in group II. They are reduced with alcohol or H_2SO_3 . The Cr^{+++} then is detected in group III.

Sulfides. In dissolving the sample in HNO_3 , sulfides may produce free sulfur or $\text{SO}_4^{=}$ ions. For sulfides soluble in HCl , the difficulty is overcome easily, but, for the nitric acid-soluble sulfides, interference is unavoidable.

Cyanides. Cyanides may form stable complex ions with elements like copper and thus prevent precipitation of sulfides. They should be avoided in student samples on account of their poisonous nature. Treatment with acids will decompose cyanides with liberation of HCN .

Ferrocyanides and Ferricyanides. The tendencies for these to react with each other and to form insoluble and difficultly filterable products lead to considerable trouble. The general method of treatment with concentrated H_2SO_4 will decompose salts of these complex cyanides.

Thiosulfates. Same as sulfites.

Thiocyanates. In the presence of iron, thiocyanates produce color interference. They can be removed by acid treatment.

Iodides. Iodides will precipitate Ag , Pb and Hg (ous) as acid-insoluble salts. They are oxidized easily by nitric acid with the liberation of free iodine. They can be removed by treatment with concentrated H_2SO_4 .

Bromides. Same as iodides.

Chlorides. Same as iodides, except that chlorine is not liberated with nitric acid.

Chlorates. Chlorates may cause oxidation, in an acid solution, of reducing substances such as the halides and nitrites. They will oxidize H_2S to sulfur. They can be removed by treatment with H_2SO_3 . It should be remembered that a violently explosive mixture is produced when a solid chlorate is warmed with concentrated H_2SO_4 .

Acetates. Acetates interfere with the regulation of the hydrogen-ion and sulfide-ion concentrations during precipitation of group II of the cations. They are removed by boiling the solution with an acid.

Nitrites. Nitrites will oxidize H_2S . They can be removed by acid treatment.

Nitrates. There is no interference when nitrates are present in dilute solution, but they oxidize H_2S when present as strong HNO_3 . They can be removed by fuming down with H_2SO_4 .

Silicates. Decomposable silicates will precipitate as silicic acid in group I. They can be removed as described on page 347.

Organic Matter. Substances like sugar, starch and organic compounds of similar nature interfere much as do tartrates and are removed by similar methods.

The means of removing these interfering substances can be summarized as follows:

1. By volatilization with acids without drastic fuming down: CO_3^- , BO_2^- , SO_3^- , S^- , CN^- , $\text{S}_2\text{O}_3^{2-}$, SCN^- , $\text{C}_2\text{H}_3\text{O}_2^-$, NO_2^- .
2. By fuming down with HNO_3 and concentrated H_2SO_4 : C_2O_4^- , F^- , $\text{C}_4\text{H}_4\text{O}_6^-$, $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Fe}(\text{CN})_6]^{3-}$, I^- , Br^- , Cl^- , organic matter, NO_3^- .
3. By reduction with H_2SO_3 : CrO_4^{2-} , ClO_3^- , AsO_4^{3-} , (MnO_4^-) .
4. By special methods: PO_4^{3-} . See page 342; for special procedure for C_2O_4^- and $\text{C}_4\text{H}_4\text{O}_6^-$ see page 342.

Preparation of the Cation Solution. The treatment of the sample, in getting it into solution and removing interfering substances, must be varied, depending on the solubility of the sample and the anions found to be present.

1. If the sample is readily soluble in dilute HNO_3 (as shown by a trial), and free from anions which require fuming down, treat a 0.05-gram portion with 1 ml. of dilute HNO_3 , and boil until completely dissolved. Use 1 ml. of this solution for the cation analysis, described on page 337.
2. If interfering anions of other types are present, proceed as follows: Treat a 0.05-gram portion of sample in a small evaporating dish with 1 ml. of dilute H_2SO_4 and 1 ml. of concentrated HNO_3 . Boil the mixture until SO_3 fumes are evolved. Add 1 ml. more of HNO_3 , and again fume down to SO_3 fumes. If tartrates are present and the solution still retains a deep brown color, repeat the acid treatment. Use 1 ml. of this solution (see page 337).

This treatment should destroy oxalates, tartrates and organic matter, as well as ferrocyanides and ferricyanides; decompose carbonates, cyanides and other volatile acids; and render soluble most of the insoluble combinations.

Comparatively few compounds are insoluble in strong HNO_3 ; hence this acid is the best solvent. Nevertheless, it will transform salts of antimony and tin into insoluble Sb_2O_5 and $\text{SnO}_2 \cdot \text{H}_2\text{O}$, which, however, are dissolved by HCl. Nitric acid will oxidize mercurous, ferrous, stannous, arsenious and antimonous compounds, and change sulfides to sulfur or to sulfuric acid with the consequent precipitation of free sulfur or of sulfates of lead, barium,

strontium and calcium. Silicic acid may be precipitated as a gelatinous residue during the treatment with nitric acid.

3. If a residue remains insoluble in concentrated HNO_3 , treat it with 1 ml. of concentrated HCl , and heat until action ceases. Add a few drops of concentrated HNO_3 if a residue still remains, thus making aqua regia the solvent; heat, dilute, and centrifuge. Unite this solution with the solutions obtained from the HNO_3 treatments, and follow the procedure outlined below for the analysis of the cations.

The residue resisting the action of all acids is referred to as the "acid-insoluble residue" and must be examined by the special methods given under "Analysis of the Insoluble Residue," page 346.

4. METALS AND ALLOYS

The alloys given out for analysis are brasses, bronzes, solders, bearing metals, type metals and steels. Alloys are classified as ferrous or non-ferrous, according to whether they consist mainly of iron or of a mixture of other metals; that is, the various kinds of iron and steels are ferrous alloys, whereas other metals predominate in non-ferrous alloys. Common carbon steels contain, besides iron, fractional percentages of carbon, phosphorus, silicon, sulfur and manganese. Alloy steels may contain, in addition to these elements, small percentages of chromium, nickel, tungsten, vanadium, molybdenum or other metals. The composition of some common non-ferrous alloys is given in the following, with the chief constituents in the order of their predominance:

Composition of Typical Alloys

Bronzes	Cu, Sn, Zn, Pb
Brasses	Cu, Zn, Sn, Pb
Solders	Bi, Sn, Pb
Solders	Zn, Cu, Sn
Auto bearing metals	Sn, Sb, Cu
Pewter	Sn, Sb, Cu, Pb, Zn
Type metals	Pb, Sb, Sn
German silver	Cu, Zn, Ni

In the systematic analysis of alloys, the metals of groups I, II and III as well as magnesium should be looked for. Among the anions only sulfides and sulfates, phosphates and arsenates and silica need be tested for.

Procedure for Dissolving the Alloy. Take about 0.05 gram of the sample in the form of turnings, drillings or chips, and treat with 1 ml. of dilute HNO_3 . Heat until brown fumes no longer are given off. Add more acid if it appears that more is necessary to dissolve the sample. In general, HNO_3 is a better solvent for most metals and alloys than HCl . HNO_3 will oxidize sulfides to H_2SO_4 , phosphides to H_3PO_4 and arsenic to H_3AsO_4 . Compounds of silicon will become silicic acid and will precipitate as gelatinous H_2SiO_3 . Tin, antimony and possibly bismuth will be precipitated as metastannic acid, H_2SnO_3 ; antimony oxide, Sb_2O_5 ; and possibly Bi_2O_3 . Carbon will remain as black specks of graphite. Some metals, like iron, aluminum and chromium, become "passive" in strong HNO_3 and dissolve very slowly.

If a white precipitate forms on treatment with HNO_3 , indicating tin or antimony, or if the sample appears to be unchanged by HNO_3 , decant the solution, saving it for analysis, and replace the HNO_3 by moderately strong HCl , heating the solution almost to boiling. If this fails to effect complete solution of the metallic portions, use aqua regia. Dilute and filter. Combine the filtrates. If silver or lead is present in the alloy, the addition of HCl will precipitate AgCl and PbCl_2 . The compounds of tin, antimony and bismuth will dissolve in HCl .

B. SYSTEMATIC ANION ANALYSIS

The procedures for the detection of anions already have been developed in Part II. They are presented here in condensed form for application to the systematic detection of anions in samples of the various types already discussed. As previously noted, it is better to carry through the analysis of the sample for anions before the cation analysis is undertaken.

The preparation of a solution of samples for anion detection of the several types already has been described. The instructions here are repeated briefly. In order to render the sample soluble, to free it from most of the metallic ions which would interfere and to maintain a strongly alkaline medium, a portion of the solid sample of about 0.05 gram is boiled in a small beaker with 0.1 to 0.2 gram of Na_2CO_3 . This treatment transposes, by double decomposition, the cations into insoluble carbonates, basic carbonates or hydroxides, which are removed by centrifuging, leaving the anions in the form of soluble sodium salts in the supernatant liquid.

This solution is referred to hereafter as the "prepared anion solution."

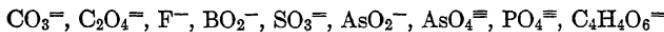
The sodium carbonate treatment is necessary, even if the sample is water-soluble, unless it is known that only sodium, potassium or ammonium salts are present. In this case, a portion of the solid sample is treated with 1 ml. of water, and then 5 drops of $\text{Ca}(\text{OH})_2$ are added. Or, if the sample is already in solution and known to contain only alkali metal salts, a portion is treated directly with $\text{Ca}(\text{OH})_2$. This treatment with base is necessary in order to prevent as far as possible the interaction of oxidizing and reducing anions which may be present in the sample. The chromate ion, in particular, may be reduced partially by the sulfite or arsenite ion, but generally enough of each remains in the basic solution to make detection possible.

The "prepared solution," now practically free from interfering cations, is then used for the detection of anions, a portion being reserved for the nitrate test as well as for a repeat analysis in case this becomes necessary. The residue is retained for special tests for phosphates, sulfides and halides, should the presence of these be suspected and not definitely identified in the prepared solution.

Detection of Carbonates. Whether or not the sodium carbonate treatment was found necessary, a test for carbonates should be made in a portion of the original sample. To carry out this test, add to a small portion of the solid or liquid sample a few drops of H_2O_2 (and 5 drops of water if the sample is solid), mix, and add a few drops of dilute H_2SO_4 . The addition of the H_2O_2 will oxidize sulfites and other ions which will produce gases. The evolution of CO_2 will be evident from the vigorous effervescence, and its presence can be confirmed with a drop of $\text{Ba}(\text{OH})_2$, according to the procedure already described (page 248).

It should be remembered further that a separate small portion of the original sample should be reserved for the nitrate test.

ANALYSIS OF GROUP I



If the color of the prepared solution or dissolved sample indicates the possible presence of chromates, procedure *b* for the precipitation of group I is to be followed; if not, procedure *a* is to be used.

Group Precipitation. (*a*) *Absence of Chromates.* To 2 ml. of the "prepared solution" or a like volume of the sample, in case the sodium carbonate treatment was unnecessary, add 5 drops of $\text{Ca}(\text{OH})_2$ and then, dropwise, about 1 ml. of the 1 M $\text{Ca}(\text{NO}_3)_2$. Heat to boiling, allow to settle, and centrifuge. Add a little more of the group reagent to the supernatant liquid to insure complete precipitation, and then boil and centrifuge. Reserve the supernatant liquid, which may contain subsequent groups. Wash the precipitate twice with water. Continue washing the residue with several drops of water, until a drop of the solution no longer gives a test for nitrates when treated with ferrous sulfate and concentrated H_2SO_4 .

(*b*) *Presence of Chromates.* Proceed as in paragraph *a* except that the solution with precipitate must not be boiled, and the washing is done with dilute NH_4OH until the washings are free from the color of the chromate ion. The residue will contain the calcium salts of members of this group. Treat precipitate with dilute $\text{HC}_2\text{H}_3\text{O}_2$, stir, and centrifuge.

Residue: CaC_2O_4 , CaF_2 . Wash thoroughly, testing washings with iodine starch. Add KMnO_4 and H_2SO_4 ; if pink color fades, oxalates are present. Add more KMnO_4 until pink remains. Add H_2O_2 until pink fades. Apply zirconium-alizarin test for fluorides.

Solution: BO_2^- , $\text{SO}_3^{=}$, AsO_2^- , $\text{AsO}_4^{=}$, $\text{PO}_4^{=}$, $\text{C}_4\text{H}_4\text{O}_6^{=}$ With separate portions test for:

Borate: Acidify a drop with HCl , dip into it, a strip of turmeric paper, dry on watch glass over boiling water. Pink color, turning green with NaOH shows borate. Confirm by flame test with alcohol.

Sulfite: Place drop of ZnSO_4 , $\text{K}_4\text{Fe}(\text{CN})_6$, and nitroprusside on spot plate. Add drop of solution → red color shows $\text{SO}_3^{=}$.

Tartrate: Char with conc. H_2SO_4 .

Arsenite: Boil several drops to remove sulfite. Add iodine starch → blue color discharged shows AsO_2^-

Arsenate: Add HCl and KI → blue color with starch shows $\text{AsO}_4^{=}$.

Phosphate: If $\text{AsO}_4^{=}$ or AsO_2^- are present, reduce remainder with Na_2SO_3 , add HCl , pass in H_2S , centrifuge, boil, add amm. molybdate → $(\text{NH}_4)_8\text{PO}_4 \cdot 12\text{MoO}_3$, yellow, shows $\text{PO}_4^{=}$.

ANALYSIS OF GROUP II



Preliminary Group Test. To a few drops of the centrifugate from group I, add a few drops of $\text{Ba}(\text{NO}_3)_2$ reagent. A precipitate shows the presence of either sulfates or chromates or both.

Detection of Sulfate. If the preliminary test showed the presence of a member of this group, take another portion of the solution, acidify it with dilute HCl, and add a few drops of the group reagent. If a white precipitate forms, it is BaSO_4 and shows the presence of SO_4^- . (The presence of the acid prevents the precipitation of BaCrO_4 .)

Group Precipitation. If the preliminary test shows the presence of group II, add slowly, with stirring, the group reagent, 1 *M* barium nitrate, until precipitation is complete. Centrifuge, and reserve the supernatant liquid for the analysis of remaining groups. The precipitate may consist of BaSO_4 or BaCrO_4 or both.

Detection of Chromate. To the residue add 4–5 drops of dilute HCl, stir, and centrifuge. Remove the supernatant liquid, which may contain chromate, to another tube. Treat this solution with dilute NH_4OH until distinctly alkaline, and then add dilute $\text{HC}_2\text{H}_3\text{O}_2$ until just acid. If chromates are present, yellow BaCrO_4 will be reprecipitated.

Centrifugate:
Group III.
Group IV.
Group V.

ANALYSIS OF GROUP III

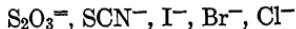


Preliminary Group Test. To a few drops of the centrifugate from group II, add a few drops of 0.5 M $Zn(NO_3)_2$. If a precipitate forms, members of this group are present. If not, pass on to group IV.

Group Precipitation. If the preliminary test showed the presence of members of this group, add slowly, with stirring, $Zn(NO_3)_2$ until precipitation is complete. Centrifuge, and reserve the centrifugate for groups IV and V. Residue may be ZnS , $Zn(CN)_2$, $Zn_2Fe(CN)_6$, $Zn_3Fe(CN)_6$ [S^- and $[Fe(CN)_6]^{=}$ cannot exist in the same sample]. Use portions for the tests below.

Sulfide. Remove a small amount of the group precipitate to another test tube, treat it with a drop of HCl, and hold in the mouth of the tube a strip of lead acetate paper. If the test paper darkens, sulfides are present in the sample.	Cyanide. Transfer the remainder of the precipitate to a small flask, add 5 ml. of water, and shake to form a suspension. Treat a piece of filter or reaction paper with NaOH, acidify the suspension with dilute HCl, and place the paper over the mouth of the flask. Heat the contents of the flask to boiling, and continue heating for half a minute. Then treat the filter paper with 2 drops of freshly prepared $FeSO_4$ solution, acidify the spot with one drop of conc. HCl, and finally add one drop of $FeCl_3$ solution. If a blue color develops, it shows the presence of CN^- .	Ferrocyanide. Remove another small portion of the group precipitate to the spot plate, acidity with a drop of dilute HCl, and add a drop of $FeCl_3$. A blue color (Prussian blue) shows the presence of $[Fe(CN)_6]^{=}$.	Ferricyanide. To a portion of the precipitate, add HCl and a drop of freshly prepared $FeSO_4$. A blue color shows the presence of $[Fe(CN)_6]^{=}$.
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ANALYSIS OF GROUP IV



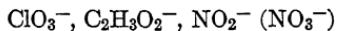
Preliminary Group Test. To about $\frac{1}{2}$ ml. of the solution, add the group reagent, a 5 per cent solution of AgNO_3 , until precipitation is complete, and then make the solution just acid with dilute HNO_3 . The presence of a precipitate indicates thiosulfates, thiocyanates, iodides, bromides or chlorides.

Detection of Thiosulfates. If during the preliminary group test the precipitate turned dark, passing through color shades of yellow, orange and red to black, the presence of thiosulfates is shown. The color change is due to decomposition of $\text{Ag}_2\text{S}_2\text{O}_3$, the final product being Ag_2S . This effect will be observed again, if thiosulfate is present, during the group precipitation.

Group Precipitation. If in the preliminary test a precipitate formed, but the thiosulfate test was negative, treat the entire solution with AgNO_3 reagent until precipitation is complete, and then heat to boiling. Then add very carefully small drops of dilute HNO_3 , with stirring, until the solution is faintly acid toward litmus; avoid an excess. Centrifuge, and wash the residue twice with a few drops of water, and add these washings to the supernatant liquid which is to be reserved for tests for anions of group V. Continue washing the residue until the washings no longer give a precipitate of AgCl with dilute HCl . The residue may contain Ag_2S , AgSCN , AgI , AgBr and AgCl .

Thiocyanate. Transfer small portion of ppt, add water and FeCl_3 . Red $\text{Fe}(\text{SCN})_6^{\text{4-}}$ shows $\text{SCN}^{\text{-}}$.	Treat remainder of precipitate with $(\text{NH}_4)_2\text{S}_2$, boil, centrifuge; again treat with $(\text{NH}_4)_2\text{S}_2$, add dilute H_2SO_4 , boil, and centrifuge; divide solution into 2 portions.
Iodide and Bromide. To a drop of the liquid, made ammoniacal with NH_4OH , add a few drops of chloroform and then NaOCl . Then add dilute $\text{HC}_2\text{H}_3\text{O}_2$, dropwise, and shake the mixture at intervals. If the chloroform layer becomes purple (I_2), iodides are present. Continue the addition of the NaOCl until the purple color is discharged. To the same tube, add a drop of H_2SO_4 , and continue to add more NaOCl . In the presence of a bromide, a brown color (Br_2) will develop in the chloroform layer.	Chloride. To second portion, add AgNO_3 until halides again have been precipitated. Centrifuge, wash, and treat precipitate with 5 drops of Miller's reagent. Centrifuge; to a drop of the centrifugate, add a drop of dilute HNO_3 . White AgCl proves chlorides.

ANALYSIS OF GROUP V



Treat centrifugate from group IV with Na_2CO_3 until it is strongly alkaline evaporate to small volume, wash, and divide the centrifugate into 3 portions

Detection of Chlorate. This test depends on the reduction of the chlorate to chloride. Conduct the test as follows: To a portion of the above solution, add dilute H_2SO_4 until slightly acid and then a few pieces of solid sodium nitrite in order to reduce the chlorate to chloride, and heat to boiling. To the boiled solution, add 2 drops of conc. HNO_3 and 2 drops of AgNO_3 . If a white precipitate (of AgCl) forms, chlorates were present in the original sample.

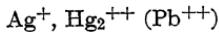
Detection of Acetate. To a portion of the solution in a crucible, add several drops of ethyl alcohol and then enough conc. H_2SO_4 to double the volume. Heat carefully. Cautiously note the odor of the warm solution. The fruity odor of ethyl acetate, which must not be confused with the odor of alcohol, shows the presence of acetates.

Detection of Nitrite. On the spot plate, place a few drops of the solution, and add a crystal of ferrous sulfate and 2 drops of acetic acid. A brown color shows the presence of nitrites.

Detection of Nitrate. Place $\frac{1}{2}$ ml. of the original sample in each of 2 centrifuge tubes. Precipitate all the insoluble barium salts by the addition of barium acetate solution to both tubes. When precipitation seems to be complete, add enough saturated silver acetate solution to precipitate all of the insoluble silver salts. Pour the contents of both tubes into a crucible, and heat the mixture to boiling. Now add a slight excess of solid Na_2CO_3 , which will remove the excess Ag^+ and Ba^{++} added in the beginning of the procedure. Heat the mixture to just below boiling, and return the contents of the crucible to the centrifuge tubes. Centrifuge, and discard the precipitate. Pour the supernatant liquid into the crucible, and add a heaping spatulaful of NH_4Cl ; now add dilute H_2SO_4 , dropwise, until all effervescence ceases, and then add a few drops in excess. Concentrate the solution to 3 or 4 ml. by heating. The solution is now ready for the ring test: To a portion of this solution, add a few crystals of FeSO_4 , warming to dissolve them if necessary. Cool under the water tap, and then add, dropwise, concentrated H_2SO_4 and again cool the tube. A brown ring forming at the junction of the two liquids shows the presence of nitrates in the sample.

C. SYSTEMATIC CATION ANALYSIS

ANALYSIS OF GROUP I



To 1 ml. of the cation solution as prepared according to the instructions on pages 321, 323, 328 and 330 from whatever type of sample being analyzed, add, dropwise, concentrated HCl with frequent stirring until precipitation appears complete. Centrifuge, test the solution for complete precipitation, and reserve it for the analysis of subsequent groups. Wash the residue several times with 3 drops of water, centrifuge after each washing, and add the washings to the solution reserved for later groups.

Precipitate: AgCl, Hg₂Cl₂, PbCl₂. Add 5 drops of water, heat, stir, centrifuge.

Centrifugate: Ions of groups II-V + excess HCl.

<i>Solution:</i> Pb ⁺⁺ . Add K ₂ CrO ₄ → <u>PbCrO₄</u> yellow. Confirm with H ₂ SO ₄ → <u>PbSO₄</u> white.	<i>Residue:</i> AgCl and Hg ₂ Cl ₂ . Treat with NH ₃ solution. Centrifuge.
<i>Solution:</i> Ag(NH ₃) ₂ Cl. Acidify with HNO ₃ . White AgCl shows silver. Confirm by "rhodanine" test.	<i>Residue:</i> Black Hg + HgNH ₂ Cl. Dissolve in aqua regia: Add SnCl ₂ ; white or gray show Hg. Confirm by diphenyl carbazide test.

ANALYSIS OF GROUP II

Hg^{++} , Pb^{++} , Bi^{+++} , Cu^{++} , Cd^{++} , AsO_2^- , AsO_4^{\equiv} , Sb^{+++} , Sb^{+++++} , Sn^{++} ,
 Sn^{++++}

Concentrate the centrifugate from group I to a volume of 1 ml. If stannous tin is likely to be present, oxidize with H_2O_2 . Adjust the acidity with methyl orange paper. Heat the solution nearly to boiling, and saturate with H_2S for 1 minute. Cool, add 10 drops of water, and again pass in H_2S . Centrifuge; test for complete precipitation. If arsenates are likely present, reduce with NH_4I , and pass in H_2S . Boil centrifugate, and reserve for groups III-V.

Precipitate may contain HgS , PbS , Bi_2S_3 , CuS , CdS , As_2S_3 (As_2S_5), Sb_2S_3 , Sb_2S_5 and SnS_2 . Wash ppt. with water containing H_2S and NH_4Cl . Centrifuge. Treat with 4 M KOH, stir, heat, centrifuge. Repeat extraction.

Centrifugate:
 Group III.
 Group IV.
 Group V.

Residue: Division A. HgS ,
 PbS , Bi_2S_3 , CuS , CdS .

See page 339.

Solution: Division B.

HgS_2^{\equiv} ;
 AsO_2^- , AsS_2^- ;
 AsO_4^{\equiv} , AsS_4^{\equiv} ;
 SbO_2^- , SbS_2^- ;
 SbO_4^{\equiv} , SbS_4^{\equiv} ;
 SnO_3^- , SnS_3^- .

See page 339.

ANALYSIS OF GROUP II, DIVISION A

Residue: HgS, PbS, Bi₂S₃, CuS, CdS. Wash with 5 drops of water. Treat with dilute HNO₃, and boil; centrifuge. Place centrifugate in a crucible.

<i>Residue:</i> HgS. Dissolve in aqua regia, boil out chlorine. Test for mercury with (a) SnCl ₂ and (b) diphenyl carbazole.	<i>Solution:</i> Pb ⁺⁺ , Bi ⁺⁺⁺⁺ , Cu ⁺⁺ , Cd ⁺⁺ . Add 5 drops of conc. H ₂ SO ₄ , boil to SO ₃ fumes. Drop solution into 10 drops of water. Centrifuge.	
<i>Precipitate:</i> PbSO ₄ . Test for lead by dissolving in (NH ₄) ₂ C ₂ H ₃ -O ₂ and adding K ₂ CrO ₄ →. <u>PbCrO₄</u> yellow.	<i>Solution:</i> Bi ⁺⁺⁺⁺ , Cu ⁺⁺ , Cd ⁺⁺ . Treat with NH ₄ OH. Centrifuge.	<i>Precipitate:</i> Bi(OH) ₃ . Test for bismuth with (a) sodium stannite Bi black and (b) cinchonine-KI <i>Solution:</i> Cd(NH ₃) ₂ ⁺⁺ . Test for copper if solution is not blue by (a) K ₄ Fe(CN) ₆ → Cu ₂ [FeCN] ₆ (b) benzoin-oxime. Cu(NH ₃) ₄ ⁺⁺ . Test for cadmium (a) copper absent: Pass in H ₂ S → (b) copper present: treat with KCN and pass in H ₂ S. → CdS yellow.

ANALYSIS OF GROUP II, DIVISION B

Centrifugate from the KOH treatment may contain the oxy- and thio-anions of arsenic, antimony and tin, and possibly mercury. Acidify with dilute HCl, centrifuge.

Precipitate: (HgS) As₂S₃, As₂S₅, Sb₂S₃, Sb₂S₅, SnS₂. Treat with concentrated HCl. Centrifuge.

<i>Residue:</i> (HgS), As ₂ S ₃ , As ₂ S ₅ . Treat with HNO ₃ . Test black residue for mercury.	<i>Centrifugate:</i> Sb ⁺⁺⁺ (SbCl ₄ ⁼); Sn ⁺⁺⁺⁺ (SnCl ₆ ⁼). Divide into two equal portions.	
<i>Solution:</i> AsO ₄ ³⁻ . Test for arsenic by (a) Gutzeit test and (b) with AgNO ₃ .	Test for antimony with (a) Rhodamine-B and (b) reduction with Zn-Pt couple.	Test for tin with (a) flame test, blue, and (b) HgCl ₂ , gray to black.

ANALYSIS OF GROUP III

This group comprises iron, manganese, chromium, aluminum, nickel, cobalt and zinc. The addition of NH_4OH will precipitate the iron, chromium and aluminum as hydroxides and most of the manganese as $\text{MnO}(\text{OH})_2$; this subgroup is designated division A. Nickel, cobalt and zinc are converted to the complex ammonia ions and referred to as division B.

Attention already has been called to the interference of anions in the systematic detection of cations. Most of the interfering anions will have been removed in the treatment of the sample prior to the analysis of group I, or otherwise taken care of. Oxalates, tartrates and phosphates, however, may be present in the solution from group II. They interfere mainly for the reason that the barium, strontium and calcium salts of these anions are insoluble in a basic solution, and, consequently, when the solution from group II is made basic with NH_4OH , these salts will precipitate along with the hydroxides of iron, manganese, aluminum and chromium. This means that, if any members of group IV, namely, barium, calcium and strontium, are contained in the sample, these alkaline earth cations will be precipitated prematurely and removed, with the ultimate result that they will escape detection in their regular places. Furthermore the presence of tartrates and similar organic substances hinders the complete precipitation of $\text{Cr}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$. Therefore, if these interfering anions have not yet been tested for, their presence or absence must be established at this point.

The test for oxalates is made as follows: Take a few drops of the solution from group II, which has been boiled previously to remove H_2S , and add Na_2CO_3 until strongly basic. Centrifuge if a precipitate forms. Make the filtrate slightly acid with $\text{HC}_2\text{H}_3\text{O}_2$, boil, and add an equal volume of saturated CaSO_4 solution. If a white precipitate (CaC_2O_4) forms, centrifuge, dissolve the residue in dilute H_2SO_4 , and add a tiny drop of very dilute KMnO_4 solution. The solution will be decolorized if oxalates are present.

Test for tartrates, sugar and similar organic material by heating a small portion of the dry sample with concentrated H_2SO_4 . A charring or blackening of the residue and the odor of burnt sugar show the presence of organic material.

Test for phosphates by taking 2 drops of the filtrate from group II, boil to remove H_2S , add a drop of concentrated HNO_3 , warm, add ammonium molybdate, and warm again. A yellow precipitate of ammonium phosphomolybdate, $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$, shows the presence of phosphates.

ANALYSIS OF GROUP III, DIVISION A: OXALATES, TARTRATES AND PHOSPHATES ABSENT

Precipitation of Division A. Concentrate or dilute centrifugate from group II to 1 ml., add 5 drops of bromine water, and boil to remove excess bromine. Add NH₄Cl, made alkaline with NH₃ solution, shake, and centrifuge. Reserve centrifugate for analysis of division B and groups IV and V. Wash twice with very dilute ammonia reagent, and add washings to main centrifugate.

<i>Residue:</i> Fe(OH) ₃ , MnO(OH) ₂ , Cr(OH) ₃ , Al(OH) ₃ . Treat with NaOH and Na ₂ O ₂ , centrifuge, and wash.		<i>Centrifugate:</i> Ni(NH ₃) ₄ ⁺⁺ . Co(NH ₃) ₆ ⁺⁺⁺ . Zn(NH ₃) ₄ ⁺⁺ . Group IV. Group V.	
<i>Residue:</i> Fe(OH) ₃ , MnO(OH) ₂ . Dissolve in HNO ₃ and H ₂ O ₂ .		<i>Solution:</i> CrO ₄ ⁼ , AlO ₂ ⁻ .	
Test portions for iron with (a) K ₄ Fe(CN) ₆ and (b) KSCN.	Test portions for manganese (a) with NaBiO ₃ and (b) by bead test.	Test portions for chromium with (a) BaCl ₂ and (b) H ₂ O ₂ .	Test portions for aluminum with (a) Aluminon and (b) Co(NO ₃) ₂ .

ANALYSIS OF GROUP III, DIVISION B: OXALATES, TARTRATES AND PHOSPHATES ABSENT

Precipitation of Division B. Pass H₂S into the centrifugate from division A until precipitation is complete. Centrifuge; wash ppt reserve supernatant solution for groups IV-V.

<i>Precipitate:</i> NiS, CoS, ZnS [MnO(OH) ₂ .] Dissolve in KClO ₃ conc. HCl. Solution may contain Ni ⁺⁺ , Co ⁺⁺ , Zn ⁺⁺ . On separate portions:		<i>Centrifugate:</i> Ba ⁺⁺ , Sr ⁺⁺ , Ca ⁺⁺ , Mg ⁺⁺ , K ⁺ , Na ⁺ , (NH ₄) ⁺ .	
Test for nickel (a) with dimethylglyoxime and (b) by bead test.	Test for cobalt with (a) α -nitroso- β -naphthol and (b) NH ₄ SCN.	Treat remainder of solution with one half its volume of 30% NaOH. Centrifuge; discard residue. Test for zinc with (a) Orange IV and (b) Rinman's green test.	
Test for manganese if not found in division A by method above.			

ANALYSIS OF GROUP III: OXALATES, TARTRATES OR PHOSPHATES PRESENT

A. If oxalates or tartrates were found, whether or not phosphates are also present, use the following procedure:

Evaporate the filtrate from group II to dryness, add a few drops of concentrated H_2SO_4 , and heat until the mass chars. Then add a few drops of concentrated HNO_3 , and heat until SO_3 fumes are evolved. Repeat the nitric acid treatment until the solution is practically clear. This treatment will destroy the oxalate and tartrate ions, but at the same time will result in the formation of insoluble $BaSO_4$, $SrSO_4$, $CaSO_4$ and possibly $Cr_2(SO_4)_3$. Cool the solution, dilute with water, transfer to a centrifuge tube, and centrifuge. The residue may consist of the sulfates of calcium, barium, strontium and possibly chromium, and the solution may contain the ions of groups III and V.

The solution now should be analyzed by the regular procedures for group III and group V.

The residue, containing the sulfates of barium, strontium, calcium (group IV) and possibly chromium now must be fused with five times its bulk of Na_2CO_3 , the melt cooled, extracted with boiling water, and centrifuged, and the residue, consisting of $BaCO_3$, $SrCO_3$ and $CaCO_3$, analyzed by the procedure for group IV. Chromium, if not found in the solution with other members of group III, should be tested for in the filtrate obtained in the removal of the above carbonates.

B. If phosphates have been found, unaccompanied by oxalates or tartrates, the procedure below is followed:

The phosphates of calcium, barium and strontium, which are insoluble in basic or neutral solutions, are precipitated along with aluminum, ferric iron and chromium, when the solution is made ammoniacal, and are not found in their regular places. The phosphates of ferric iron, aluminum and chromium are insoluble in weak ferric acid; those of calcium, barium and strontium are soluble in this weakly acidic solution. If the phosphate is precipitated with Al^{+++} , Cr^{+++} or Fe^{+++} ions, the alkaline earth cations will remain in the filtrate and can be detected in their regular places. In order to insure complete precipitation of the phosphates, ferric ions in the form of $FeCl_3$ are added in excess, as the quantity of the phosphates present in the sample may be in excess of the Al , Fe^{+++} and Cr^{++} ions present. The excess Fe^{+++} ions over those necessary to precipitate the $PO_4^{=}$ ions are removed by the formation of basic ferric acetate, $Fe(OH)_2C_2H_3O_2$.

After phosphates are shown to be present, the next step is to test for iron. Place a drop of the filtrate from group II on a spot plate with a drop or two of H_2O_2 to oxidize the iron to the ferric state, and then add a drop of KCNS. A deep red color shows the presence of iron. This test for iron is necessary at this point, because $FeCl_3$ is added later to precipitate the phosphate completely.

Boil the filtrate from group II to remove H_2S , make just ammoniacal with NH_4OH , and then add enough dilute HCl to make the solution slightly acid. Add solid $NH_4C_2H_3O_2$ and 2 drops of 50 per cent $HC_2H_3O_2$. If sufficient iron is present to precipitate all the phosphate as $FePO_4$ and still leave the solution red, there will be an excess; otherwise, add $FeCl_3$ solution, dropwise, until the

solution turns red. The red color is due to $\text{Fe}(\text{C}_2\text{H}_3\text{O}_2)_3$. Dilute the solution with about 10 drops of water, and heat to boiling. The boiling will precipitate the excess iron as $\text{Fe}(\text{OH})_2\text{C}_2\text{H}_3\text{O}_2$.

The precipitate may consist of FePO_4 , AlPO_4 , CrPO_4 and $\text{Fe}(\text{OH})_2\text{C}_2\text{H}_3\text{O}_2$, and all the phosphate will have been removed from solution. Test the filtrate for the presence of the phosphate ion in the manner mentioned. When the phosphates are shown to be completely removed, analyze the filtrate for Mn^{++} , Ni^{++} , Co^{++} , Zn^{++} , Ca^{++} , Ba^{++} and Sr^{++} and group V, according to the regular procedure.

ANALYSIS OF GROUP IV

Ba^{++} , Sr^{++} , Ca^{++}

Transfer the centrifugate from group III to a crucible, place the crucible on a triangle, and carefully concentrate the solution by boiling until salt crystals begin to form. Remove the flame, and add 15–20 drops concentrated HNO_3 from a dropper, flushing down the sides of the crucible. Under the hood, evaporate the solution to dryness, cautiously playing the flame around the crucible to prevent spattering. Finally, heat the residue until ammonia fumes no longer are given off. After the crucible has cooled, add about 1 ml. of water to which 1 drop of dilute HCl has been added. Place the solution in a centrifuge tube. If the solution is not clear, centrifuge, and discard the residue. Add 10 drops of NH_4Cl solution, 1 drop of NH_3 solution and, dropwise, enough $(\text{NH}_4)_2\text{CO}_3$ to effect complete precipitation. Centrifuge.

Precipitate: BaCO_3 , SrCO_3 , CaCO_3 . Wash with 5 drops of water. Treat with dilute $\text{HC}_2\text{H}_3\text{O}_2$. Add $\text{NaC}_2\text{H}_3\text{O}_2$ and K_2CrO_4 . Centrifuge.

Centrifugate:
Group V,
 Mg^{++} , Na^+ ,
 K^+ , NH_4^+ .

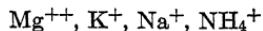
Centrifugate: Sr^{++} , Ca^{++} . Make alkaline with NaOH , heat in water bath, add Na_2CO_3 , centrifuge, dissolve SrCO_3 and CaCO_3 in $\text{HC}_2\text{H}_3\text{O}_2$. Add $(\text{NH}_4)_2\text{SO}_4$. Centrifuge.

Precipitate: BaCrO_4 . Dissolve in conc. HCl . Apply flame test.

Residue: SrSO_4 (CaSO_4). Boil with Na_2CO_3 , centrifuge, dissolve in HCl , and apply flame test for strontium.

Centrifugate: Ca^{++} . Add $(\text{NH}_4)_2\text{C}_2\text{O}_4$. Apply flame test.

ANALYSIS OF GROUP V



To the centrifugate from group IV, add 1 drop of $(\text{NH}_4)_2\text{SO}_4$ and 1 drop of $(\text{NH}_4)_2\text{C}_2\text{O}_4$; centrifuge if a precipitate forms; discard the precipitate. Transfer the solution to a crucible, and remove ammonium salts as directed in group IV. Divide into 3 portions.

<i>Portion 1.</i> Test for magnesium by taking a drop of the solution, adding a drop of the α -nitrobenzene-azo resorcinol reagent and making alkaline with NaOH. A blue color shows magnesium. Confirm by the phosphate test as described on page 88.	<i>Portion 2.</i> Test for potassium by placing a drop of the solution on a spot plate and adding $\text{Na}_3\text{Co}(\text{NO}_2)_6$. A yellow precipitate shows potassium. Confirm by flame test.	<i>Portion 3.</i> Test for sodium by placing a drop of the solution on a centrifuge tube and adding 8 drops of the zinc uranyl acetate reagent. A pale yellow precipitate shows sodium. Confirm by flame test as observed while conducting the flame test for K.
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Test for Ammonium Ion. Use a separate portion of the original sample, and conduct test as described on page 53.

D. THE ANALYSIS OF THE INSOLUBLE RESIDUE

In preparing a solution for the systematic detection of cations, the treatment of the sample with acids frequently will leave a residue of insoluble constituents which resist the action of HNO_3 and HCl , taken singly or in combination as aqua regia. Such insoluble compounds may have been constituents of the original sample or may have been formed by interaction of the ions of soluble components. This residue must be examined before the sample can be considered to be completely analyzed.

An inspection of the solubility table shows that comparatively few substances resist the action of hot concentrated HNO_3 . The list includes BaSO_4 , SrSO_4 , (CaSO_4), PbSO_4 ; the halides of silver and possibly those of lead and mercurous mercury; the sulfides of mercury; the cyanogen compounds of silver and certain other metals; gelatinous silicic acid from decomposable silicates; oxides of tin and antimony. Free sulfur may result from the action of nitric acid on sulfides, and black specks of carbon may be derived from organic matter.

The action of aqua regia following that of nitric acid will dissolve the oxides of antimony and tin and the sulfides of mercury, and will transpose, at least partially, the silver halides and complex cyanogen salts into AgCl .

The residue then may consist of the following substances:

PbSO_4 , (PbCl_2).

AgCl , (AgBr , AgI , AgCN , AgCNS , $\text{Ag}_3\text{Fe}(\text{CN})_6$,
 $\text{Ag}_4\text{Fe}(\text{CN})_6$).

BaSO_4 , SrSO_4 , (CaSO_4).

H_2SiO_3 , (SiO_2 , silicates).

Sulfur, carbon.

Proceed with the systematic analysis of this residue as follows:

1. Digest a portion of residue with hot $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ solution to dissolve any PbCl_2 and PbSO_4 which may be present. Examine the filtrate for Pb^{++} , Cl^- and SO_4^- ions.

2. Treat a portion of the residue with NH_4OH . This will dissolve AgCl and some AgBr , and silver thus can be tested for in the filtrate by acidifying it with HNO_3 .

3. Roast a portion of the residue in an open dish if particles of black carbon or yellow sulfur are visible. These will be oxidized and removed as CO_2 and SO_2 .

4. Mix the roasted residue with 10 times its weight of an equal mixture of Na_2CO_3 and K_2CO_3 in a porcelain crucible, and heat over a blast lamp or Méker burner until the fused mass becomes a clear melt. Place the cool crucible in a beaker, cover with water, and boil. Crush the residue with a stirring rod. Filter, and wash the residue. Test for sulfates in the filtrate by acidifying with HCl and adding BaCl_2 ; a white precipitate of BaSO_4 proves the presence of $\text{SO}_4^{=}$. Dissolve a portion of the washed residue with dilute HCl, and test for the alkaline earth ions in the resulting solution. Add HNO_3 to another portion of the residue, if dark colored, to dissolve metallic silver, and test for silver in the filtrate.

SPECIAL ANALYSIS OF SILICATES

The abundance of silicates in minerals, rocks, clays and soils, as gangue in ores and as constituents of many artificial products, makes their analysis important enough for a section to be devoted to their special consideration.

Only the alkali silicates are soluble in water. Some silicates are decomposed by acids, rendering the silicate ion insoluble as gelatinous silicic acid, H_2SiO_3 or $\text{SiO}_2 \cdot x\text{H}_2\text{O}$, where the silica can be tested for by the metaphosphate bead test, and dissolving the metal constituents as chlorides or nitrates where they can be detected by the usual methods of cation analysis. Most silicates, however, are not acted upon by mineral acids and require either a fusion or a treatment with hydrofluoric acid to render them soluble.

PROCEDURES FOR SILICATE ANALYSIS

Take a 0.05-gram portion of the finely ground sample, mix it with 1 gram of equal parts of Na_2CO_3 and K_2CO_3 and $\frac{1}{2}$ gram of KNO_3 , and place the mixture in a platinum crucible, unless easily reducible metals such as Sn, Sb, Bi, Ag and Pb are likely to be present, in which case a nickel or a porcelain crucible must be used. Heat the crucible over a blast lamp until the melt is clear and ceases bubbling. This action will convert the silicate into soluble sodium silicate and the metals into carbonates, oxides or other forms.

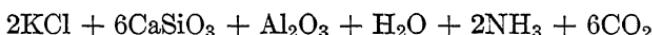
Cool the crucible, place it in an evaporating dish, and cover with dilute HCl. Remove the crucible, crush any lumps that may be present, and evaporate the solution to dryness. Bake the residue

to dehydrate the silicic acid, extract with hot HCl, dilute, and filter off the SiO₂. Examine the residue by the metaphosphate bead test, and test the filtrate for cations by the usual procedure.

Alternate Method. Take a 0.05 sample, place it in a platinum crucible, add 10 ml. of HF acid and a few milliliters of concentrated H₂SO₄, and warm *in the hood*. Evaporate until dense white fumes of SO₃ appear. This treatment will decompose any silicate, evolving the silicon as SiF₄ and leaving the metals as sulfates. Extract with water, filter if necessary, and examine the filtrate for cations and the residue for such metals as barium, strontium and calcium.

Of special interest in the analysis of silicates is the detection of potassium in minerals such as feldspar, because by geological weathering processes this potash became available as a valuable plant food. Potassium may be detected in the filtrate from the hydrofluoric acid treatment, but a better method is to apply a special fusion. This is known as the J. Lawrence Smith method and is carried out as follows:

Mix a half-gram portion of the finely ground feldspar with an equal weight of NH₄Cl (alkali-free) and about 5 grams of pure CaCO₃. Place the mixture in a high covered platinum crucible, and heat to a dull redness for at least half an hour. The action may be shown approximately by the equation:



although the effective fusion agent above is doubtless CaCl₂ which is formed by the interaction of NH₄Cl with CaCO₃.

Allow the crucible to cool, transfer it to an evaporating dish, boil, filter, remove the excess calcium with (NH₄)₂CO₃, and examine the final filtrate for potassium.

APPENDIX A

COLLOIDS

The Colloidal State. In a true solution, the solute is present in particles of molecular or ionic size, about 10^{-8} cm. in diameter. If the solute particles are larger, but not so large that they settle out on standing for a reasonable length of time, they are said to be in the colloidal condition, and the mixture is a colloidal system. The limits of size of colloidal particles may be placed arbitrarily at diameters between 10^{-4} and 10^{-7} cm.

For convenience, liquid colloidal systems may be divided into two general classes—sols and gels—although there is no sharp distinction between the two. The terms suggest the general characteristics of the systems: sols are similar to solutions (low viscosity, filterable, and so forth, and gels resemble jellies; in fact, jellies are gels. Although some compounds, such as the hydroxides of iron and aluminum, precipitate as gels, this type of colloidal system occurs less frequently in qualitative analysis than the sol type.

Sols, however, are of considerable importance, primarily because of our desire to avoid them. The dispersed particles in sols cannot be removed by filtering and usually not by centrifuging for a reasonable length of time; consequently, sol formation may make an analytical separation incomplete or impossible. Sol formation is particularly undesirable in the semi-micro method, because of the small amounts of materials used and the extreme sensitivity of some of the tests to contaminating ions.

The suspended particles in sols all carry either positive or negative electric charges; that is, sol particles are essentially gigantic ions. The charges arise in either of two general ways: (1) adsorption of ions from the solution onto the surface of the sol particle; or (2) partial ionization of some component of the sol particle, the ions of one sign going into the solution and the ions of opposite sign remaining on the sol particle. Whatever the origin of the charges, they cause the sol particles to repel each other, thus tending to prevent collisions and consequent coagulation of the sol.

The charges, then, stabilize the sol. If these charges can be removed or decreased sufficiently, the sol particles will collide more frequently, and coagulation will occur.

Heating tends to remove the adsorbed ions and hence encourages coagulation. If ions of charge opposite to that of the particle are adsorbed in sufficient numbers, they will neutralize effectively the charge of the particle and consequently produce coagulation. Therefore, the addition of an ionized compound to the system sometimes will bring about precipitation of the sol.

An apparently obvious objection to this method of precipitating a sol is the impossibility of adding negative ions to a positively charged sol without adding, at the same time, an equivalent number of positive ions. The latter might reasonably be expected to aid in stabilizing the sol and thus counteract the coagulating effect of the negative ions. The same argument holds, of course, for negative sols and positive coagulating ions. This stabilizing effect, although it undoubtedly exists, is, however, of less significance than the coagulating tendency of the oppositely charged ions.

A very important factor in determining the coagulating power of an ion is the number of units of charge that it carries. The coagulating ability increases greatly with increase in the charge. Thus, aluminum compounds are much more effective than magnesium compounds, which in turn are more effective than sodium compounds in coagulating negative sols; similarly phosphates, sulfates and chlorides have decreasing abilities, in the order named, to coagulate positive sols.

As far as application in a scheme of analysis is concerned, however, this charge effect usually cannot be utilized, because divalent and trivalent ions, if added, almost always will produce unwanted precipitations or other reactions. Hydrogen and hydroxyl ions are much more effective than other monovalent ions and are commonly used to coagulate colloidal particles. NH_4NO_3 and NH_4Cl are the salts most frequently used to destroy colloidal suspensions, because, although they are not so effective as other salts, they do not complicate the usual scheme of analysis. The addition of these compounds to the water used to wash precipitates tends to prevent the precipitate from going into the colloidal condition. Frequent use is made of this fact in the schemes of analysis.

Colloidal systems may be formed spontaneously in precipitations or in oxidation-reduction reactions, especially in those in-

volving the formation or dissolving of sulfides. Thus, the addition of H_2S to a solution containing ions of a metal which forms a slightly soluble sulfide frequently will produce a colloidal suspension of the sulfide, especially if the solution is alkaline. The sulfide sol is stabilized by the adsorption of H_2S , hydrosulfide or sulfide ions (the latter two are present in high concentration in an alkaline solution), but usually may be coagulated by increasing the acidity of the system, provided, of course, the increased acidity does not cause the precipitate to redissolve. Similarly, the oxidation of H_2S or a sulfide, or the acidification of a polysulfide usually results in the formation of a white colloidal suspension of sulfur which may be very hard to eliminate.

In the analytical scheme, sulfur suspensions are obtained almost invariably in (a) precipitating group II of the cations if any oxidizing agents are present, (b) dissolving the group IIA sulfides in HNO_3 and (c) reprecipitating Group IIB sulfides by acidifying the solution. When very strong oxidizing agents are used, some of the sulfur is oxidized to the sulfate form but it is difficult to eliminate all of it in this way.

Up to this point, we have said less about gels than their importance merits. Gels and sols differ not in type but only in degree. Many compounds which easily form sols can be obtained in the form of gels by the use of appropriate techniques. For instance, $BaSO_4$, as usually precipitated, forms a sol, but, if saturated solutions of $Ba(SCN)_2$ and $MnSO_4$ (the most soluble barium salt and the most soluble metallic sulfate) are mixed, a gel of $BaSO_4$ is obtained; this gel is so viscous that it cannot be poured from the container.

One of the factors determining whether a given precipitation process will result in the formation of a sol or a gel is the rate of formation of nuclei of the precipitate; if the rate of formation is very high, a gel will result, and if it is relatively low, a sol will be formed. The rate of nuclei formation will be higher if the concentrations of the precipitating solutions are greater and the solubility of the precipitate is lower. Consequently, gel formation may be minimized by the carrying out of precipitations slowly, at the boiling point, using solutions that are not too concentrated. These conditions discourage the formation of any type of colloidal system.

Some precipitates, however, are gelatinous, even if all the foregoing conditions are observed. Among these are the hydrox-

ides of iron, aluminum and chromium. These form gels, because their solubility is so exceedingly low that this factor outweighs all the others.

To speak of gelatinous precipitates in general, and of the aforementioned hydroxides in particular, as definite chemical compounds is a type of chemical fiction. It is doubtful whether a compound such as, for example, Fe(OH)_3 actually exists; if it does, it is not the reddish gelatinous material to which this formula usually is applied. The so-called ferric hydroxide is really a hydrated oxide of indefinite composition, perhaps best represented by the formula $\text{Fe}_2\text{O}_3(\text{H}_2\text{O})_x$, or possibly by FeOOH . The same is true of most "hydroxides" of trivalent and tetravalent metals; so, when the student encounters such formulas as Al(OH)_3 and Mn(OH)_4 , he should interpret them as meaning "hydrated Al_2O_3 " and "hydrated MnO_2 ."

EXPONENTS AND LOGARITHMS

EXPONENTS

The labor of counting figures to the left or right of the decimal point can be eliminated by the use of exponents. In addition to economy of space, a glance at the exponent gives an immediate insight into the magnitude of the number. In data concerning solubility and equilibrium constants, and, in general, in many of the data of the exact sciences, even though the magnitudes may be extremely large or small, the values seldom are obtained with a precision extending even to the fourth significant figure.

The magnitude of a quantity is expressed in the exponential form by writing the digits as coefficients multiplied by 10 raised to the proper power. Thus, the number 1000, which is the product of $10 \times 10 \times 10$, or ten cubed, is written exponentially 1×10^3 . The number 0.001, the product of $0.1 \times 0.1 \times 0.1$, is written 1×10^{-3} . The number 7000 becomes 7×10^3 , and 0.007 becomes 7×10^{-3} . The simple rules for exponents and coefficients in converting ordinary numbers into the exponential form are these:

1. For numbers greater than unity, the exponent acquires the same value as the number of zeros in the ordinary number. In the example given, three zeros are found; therefore the exponent is 3.
2. For numbers less than unity, that is, for decimal fractions, the exponent, with a negative sign, is one more than the number

of zeros which follow the decimal point. In converting the number 0.007, the exponent is -3 .

3. According to the convention adopted in this book, the coefficients are treated in the following manner. When more than one significant figure is given, followed or preceded by zeros, the first significant figure is placed before the decimal point; the other significant figures follow the decimal point. In view of this convention in the location of the decimal point, the value of the exponent must be adjusted. For example, the number 504000, when expressed according to rule 1, is 504×10^3 , but, according to the convention of placing one significant figure to the left of the decimal point, the quantity is written 5.04×10^5 . Likewise, the number 0.000504 becomes 5.04×10^{-4} .

By the use of the exponential form of expression, the arithmetical operations of multiplication, division, and so on are greatly simplified.

Multiplication by Use of Exponents. To multiply two or more quantities, first express the numbers exponentially, then multiply the coefficients in the ordinary way, and add the exponents algebraically.

Example 1. Multiply 45,000 by 0.051.

Since 45,000 becomes 4.5×10^4 , and 0.051 becomes 5.1×10^{-2} by multiplying the coefficients and adding the exponents we obtain

$$\begin{aligned} 45,000 \times 0.051 &= (4.5 \times 5.1)10^{4-2} \\ &= 22.95 \times 10^2 \\ &= 2.295 \times 10^3 \end{aligned}$$

Division by Use of Exponents. To divide one quantity by another, express them in exponential form, divide the coefficients in the ordinary manner, and subtract the exponents algebraically.

Example 2. Divide 3730 by 15.21.

$$\begin{aligned} \frac{3730}{15.21} &= \frac{3.73 \times 10^3}{1.521 \times 10^1} \\ &= 2.45 \times 10^2 \end{aligned}$$

When numbers are to be raised to any required power, the exponents are doubled for squaring, trebled for cubing, and so on, the coefficients being squared, cubed, and so forth in the ordinary way.

Example 3. Square the number 6.0×10^3 .

$$\begin{aligned}(6.0 \times 10^3)^2 &= (6 \times 10^3) \times (6 \times 10^3) \\&= (6 \times 10^3)^2 \\&= 36 \times 10^{3 \times 2} \\&= 36 \times 10^6 \\&= 3.6 \times 10^7\end{aligned}$$

To extract the square root, divide the exponent by 2, and to extract the cube root, divide the exponent by 3, treating the coefficients in the usual manner. If the exponent is an odd number, increase it by 1, and compensate for this in the coefficient.

Example 4. Extract the square root of 1.6×10^{-5} . When this is changed to an exponential value with an even exponent,

$$\begin{aligned}\sqrt{1.6 \times 10^{-5}} &= \sqrt{16 \times 10^{-6}} \\&= 4 \times 10^{-3}\end{aligned}$$

The extraction of roots becomes a comparatively simple matter when logarithms are used, as explained on page 356.

LOGARITHMS

The use of logarithms not only greatly facilitates computations and effects a considerable saving of time and labor, but also is indispensable in certain types of chemical calculations. Though no doubt the student has had occasion to use logarithms in his courses in mathematics, a brief discussion is given here for review.

A logarithm is an exponent which must be applied to a number taken as a base in order to produce any given number. In the system of common or Briggsian logarithms the base is 10. Thus in the equation,

$$1000 = 10^3$$

the exponent 3 is the common logarithm of 1000 to the base 10, or, expressed in terms of logarithms, $\log_{10} 1000 = 3$.

In the equation

$$0.001 = 10^{-3}$$

the common logarithm of 0.001 is -3 . The logarithm of 10 or 10^1 is 1, and for 1 or 10^0 it is 0. Note that in these examples the ex-

ponents are given in whole numbers, with no significant figures following the decimal point. If, however, the exponent consists partly of a decimal fraction, as in the equation,

$$217 = 10^{2.3365}$$

the logarithmic equation is

$$\log_{10} 217 = 2.3365$$

giving the logarithms to four significant decimal places. Table XXVII shows the relation between exponents and logarithms.

TABLE XXVII

<i>Number</i>	<i>Exponential Form</i>	<i>Logarithm</i>
1,000,000	10^6	6
1,000	10^3	3
100	10^2	2
10	10^1	1
1	10^0	0
0.1	10^{-1}	-1
0.01	10^{-2}	-2
0.001	10^{-3}	-3
0.000001	10^{-6}	-6

A logarithm is made up of two parts: the *mantissa*, placed to the right of the decimal point, and found in logarithmic tables; and the *characteristic*, placed to the left of the decimal point. The mantissa gives the *antilogarithm*, or the number of which it is the logarithm; the characteristic locates the decimal point in the antilogarithm. Thus the logarithm of 217 is 2.3365, where 2 is the characteristic and 0.3365 is the mantissa. In four-place tables of logarithms, the mantissa is given to four significant places. The following rules apply in determining the characteristic.

1. If there are n digits before the decimal point, the characteristic is represented by a number equal to $n - 1$. Thus the number 217 has $3 - 1$ or 2 as the characteristic of its logarithm.
2. If there are no digits before the decimal point and no zeros before the significant figures after the decimal point, the characteristic is $\bar{1}$, or $9 - 10$. If there are no digits before the decimal point and n zeros before the first significant figure after the decimal point, the characteristic is $\bar{1} + (-n)$ or $(9 - n) - 10$. It is to be noted that the characteristic only is affected by the negative sign, the mantissa retaining a positive value.

The following examples illustrate the use of the logarithm tables in finding logarithms.

Example 5. Find the logarithm of 5326.

The characteristic is 3, since there are 4 digits before the decimal place. In the table of logarithms in the Appendix, locate 53 in the "natural numbers" column, and move horizontally to the right until, under the "2" column, the figures 7259 are found. This is the mantissa of 5320. By moving farther to the right along the same line, the figure 5 is found under column 6 of "proportional parts." This figure, 0005, shows how much greater the logarithm of 5326 is than that of 5320. The logarithm of 5326 is therefore $3.7259 + 0.0005$ or 3.7264.

Example 6. Find the logarithm of 0.0002457.

The characteristic is $\bar{4}$ or $6 - 10$. The mantissa is found by locating 24 in the "natural numbers" and moving horizontally to the "5" column. To the figure there found, 3892, must be added the proportional part under "7," giving 3904 as the value for the mantissa. The logarithm is therefore $\bar{4}.3904$ or $6.3904 - 10$.

Use of Logarithms in Mathematical Operations. The operations of multiplication and division and their extensions to raising numbers to any desired power or conversely in extracting roots are accomplished most readily by the use of logarithms. For multiplication and division, the process consists in converting the given numbers to their logarithms, then performing the indicated addition or subtraction, and finally converting the sum or difference of the logarithms to ordinary numbers. Finding the number corresponding to a logarithm is obviously the reverse of the process of finding a logarithm. This involves the use of a table of antilogarithms and is illustrated in the following example.

Example 7. Find the antilogarithm of 2.1768.

Using the table of antilogarithms in the Appendix, locate the number 17 in the "logarithms" column. Move horizontally to the "6" column, where 1500 is found. Move farther to the right until column 8 under "proportional parts" is reached. The figure there found, 3, is added to 1500, giving 1503. The characteristic 2 means that there are three digits to the left of the decimal point. The required number is therefore 150.3.

Extraction of Square and Cube Roots. The simplest manner of extracting square and cube roots is by the use of logarithms. Since logarithms are exponents, the rules given in the section on expo-

nents will govern the method used. This is illustrated by the following examples.

Example 8. Find the square root of 504.7.

The logarithm of 504.7 is 2.7030. Dividing this logarithm by 2 gives 1.3515, the logarithm of the square root. The desired number is, therefore, 22.5.

Example 9. Find the cube root of 0.0356.

The logarithm of 0.0356 is $\bar{2}.5514$ or $8.5514 - 10$. It is desirable on division to obtain a quotient which will retain the quantity -10 . Hence, the logarithm is adjusted to $28.5514 - 30$. Division by 3 gives the value $9.5171 - 10$. The antilogarithm, the cube root of 0.0356, is 0.329.

Interconversion of Exponential Numbers. It is sometimes desired to express quantities in the exponential form so that the coefficient shall be 1. This transformation necessitates the use of logarithms. Calculations of this kind are illustrated in the following examples.

Example 10. Express the quantity 6.2×10^4 in the pure exponential form.

In order to transfer the coefficient, 6.2, to the exponent, the logarithm of 6.2 is added to the logarithm of 10^4 .

$$\begin{aligned}\log (6.2 \times 10^4) &= \log 6.2 + \log 10^4 \\ &= 0.7924 + 4 \\ &= 4.7924 \\ &= 4.8\end{aligned}$$

From the fact that logarithms are exponents it is obvious that

$$6.2 \times 10^4 = 1 \times 10^{4.8}$$

Example 11. Convert 7.2×10^{-5} to the pure exponential form.

$$\begin{aligned}\log (7.2 \times 10^{-5}) &= \log 7.2 + \log 10^{-5} \\ &= 0.8573 + (-5) \\ &= -4.1\end{aligned}$$

Therefore

$$7.2 \times 10^{-5} = 1 \times 10^{-4.1}$$

The reverse process affords no difficulties when positive exponents are involved, but the operation is somewhat more compli-

cated with negative exponents. Suitable examples of both types follow.

Example 12. Express $1 \times 10^{6.45}$ as a mixed number.

In the quantity $1 \times 10^{6.45}$, the exponent 6.45 is a logarithm with a characteristic of 6 and a mantissa of 0.45. In order to retain in the exponent the whole number 6, it is necessary to find the antilogarithm of 0.45 and use it as the coefficient.

From the antilogarithm tables, the antilogarithm of 0.45 is 2.8. Therefore,

$$\begin{aligned} 1 \times 10^{6.45} &= 1 \times 10^{0.45} \times 1 \times 10^6 \\ &= 2.8 \times 10^6 \end{aligned}$$

Example 13. Convert $1 \times 10^{-7.63}$ into a mixed number.

In the discussion of characteristics of logarithms, it was stated that the mantissa must have a positive value. In the exponent or logarithm -7.63 , the mantissa as well as the characteristic is negative, and, in order to convert the value -0.63 into a positive mantissa, 0.63 is subtracted from 1.00, giving as a positive mantissa 0.37 and -8 as the new characteristic, or

$$1 \times 10^{-7.63} = 1 \times 10^{-8} \times 10^{0.37}$$

From the antilogarithm table it follows that

$$10^{0.37} = 2.3$$

The converted quantity now can be expressed as a mixed number, with a positive coefficient and an exponent consisting of a negative whole number. Therefore,

$$1 \times 10^{-7.63} = 2.3 \times 10^{-8}$$

The calculation of pH values involves the finding of the logarithm of reciprocals. Here, the expression of quantities in the pure exponential form is often highly desirable. The following examples illustrate the method of procedure.

Example 14. Calculate the value of $\log \frac{1}{1 \times 10^{-6}}$.

$$\begin{aligned} \log \frac{1}{1 \times 10^{-6}} &= \log 1 - \log 10^{-6} = -\log (1 \times 10^{-6}) \\ &= 0 - (-6) \\ &= 6 \end{aligned}$$

Example 15. Calculate the value of $\log \frac{1}{7.2 \times 10^{-5}}$.

$$\log \frac{1}{7.2 \times 10^{-5}} = \log 1 - \log (7.2 \times 10^{-5}) = -\log (7.2 \times 10^{-5})$$

From example 12, the value of $\log (7.2 \times 10^{-5})$ is -4.1 or

$$\begin{aligned}\log \frac{1}{7.2 \times 10^{-5}} &= 0 - (-4.1) \\ &= 4.1\end{aligned}$$

It often is desired to accomplish the reverse of the foregoing process, that is, to determine hydrogen-ion concentrations from the corresponding pH values.

Example 16. If $\log \frac{1}{C} = 9.63$, find the value of C .

$$\log \frac{1}{C} = 9.63$$

$$\log C = - \left(\log \frac{1}{C} \right) = -9.63$$

$$= 10.37 - 20 \text{ or } \overline{10.37}$$

$$C = 2.3 \times 10^{-10}$$

Example 17. Calculate K if $\log \frac{1}{K} = -25.76$.

$$\log \frac{1}{K} = -25.76$$

$$\log K = 25.76$$

$$K = 1 \times 10^{25.76}$$

$$\text{or } K = 5.8 \times 10^{25}$$

APPENDIX B

SUGGESTIONS TO THE INSTRUCTOR

The planning of the course, the procuring of the necessary equipment, reagents, and the like, and the general administration of the laboratory work, naturally, will depend upon the existing facilities, the time allotted for laboratory instruction, and the enrollment in the one or more laboratory sections. Here only the most general hints can be given, based on the authors' experience.

Arrangement of Reagents. Each student should have, as his personal kit, a reagent block with drilled holes to carry (1) the solid reagents contained in the small biological vials (24); (2) the test papers in suitable vials (6); (3) the commonly used reagents such as acids and bases, contained in 30-ml. bottles with droppers (12); and (4) the 12 centrifuge tubes which also serve as test tubes and for which this block serves as a test-tube holder as well. Such a block may be best made by the local carpenter shop and may have dimensions best suited for the locker.

Likewise, each student should be supplied with a set of 8-ml. screw-cap vials with dropping tubes for his personal set of liquid reagents. These are contained in another reagent block. The instructor should decide in advance what reactions described under "Preliminary Experiments" may be omitted, as well as what reagents are best dispensed personally as needed, such as H_2PtCl_6 , deducting these from the total list given under "Liquid Reagents." Excepting the reagents to be contained in the larger 30-ml. bottles, the total is about 48.

Upon checking in, the student may well label the vials and fill them from the general supply, thus relieving the staff of a burdensome task.

Lastly, the test solutions of the cations and anions require disposition. Tables and instructions are given here in the Appendix for the preparation of stock solutions (10 milligrams per milliliter). For the students' use it has been found more practicable to place at convenient locations on the laboratory tables sets of these solutions, contained in 30-ml. bottles with droppers, rather than to require each student to keep an individual set in his locker.

Centrifuges. One centrifuge may be used by several students, and, if necessary, as many as five students may be assigned to the same instrument. This depends upon the arrangements of the laboratory. Preferably, the centrifuges should be installed within reach of the student's working place. Hand-driven centrifuges are not recommended, since under rough treatment the bearings wear out. Nor are the angle centrifuges recommended, because the precipitate tends to accumulate along the sides rather than completely at the apex, thus making removal of the supernatant liquid more difficult. The instrument best suited, in the authors' experience, is an electrically driven horizontal-whirl centrifuge now procurable from a leading supply house.

SUGGESTED WEEKLY SCHEDULE

<i>Week</i>	<i>Laboratory:</i> <i>Two 3-Hour Periods</i>	<i>Class Room: Two 1-Hour Periods, Lectures and Recitation</i>	<i>Home Assignments</i>
1	Check in Reagent assembly	Introductory lecture Reagents Chapter I	Questions and Problems, Set 1 (Reagents)
2	Alkali metals Na, K, NH ₄ Start group IV	The Theory of Solutions Chapter II Reactions of Groups V and IV	Q and P, Set 2 (Molar concentrations) Review Exercises V (Cations)
3	Alkaline earths Ba, Sr, Ca, Mg Sample I Groups IV, V	The Theory of Precipitation Chapter III	Q and P, Set 3 (Solubility Product) Review Exercises IV (Cations)
4	Group IIIA Fe, Mn, Al, Cr Group IIIB Ni, Co, Zn	<i>Redox</i> Theory; Amphoterism Chapter IV Reactions of Group III or/and <i>Redox</i> equations	Q and P, Set 4 (Balancing <i>Redox</i> Equations) Review Exercises IIIA (Cations)
5	Sample 2 Unknown group III Sample 3 Groups III, IV, V	The Theory of Complex Ions Chapter IVB	Q and P, Set 5 (Calc. Instability Constants) Review Exercises IIIB (Cations)
6	Group I *Ag, Hg(ous), Pb Bi, Cu, Cd	Ionization Equilibria and Common-ion Effect Chapter VA	Q and P, Set 6 (Ionization Constants) Review Exercises I (Cations)
7	Sn, Sb, As Sample 4 Group I-II	Buffered Precipitation. Theory of Sulfide Precipitation Chapter VB	Q and P, Set 7 (Buffer Calculations Controlled Precipitation) Review Exercises IIIA (Cations)

8	Sample 5 Groups II, III Sample 6 All groups. Gen- eral cation sample	General review (Midsemester exam)	Review Exercises II B (Cations)
9	Anion Group I Cont. or sample 7 Anion Group I	Chapter VI <i>pH</i> Reactions of Anions of Group I or <i>pH</i> Calcu- lations	Q and P, Set 8 (<i>pH</i> Calculations) Review Exercises I (Anions)
10	Anions II, III Groups I, II, III	The Theory of Neutralization and Hydrolysis Chapter VII Hydrolysis Calculations	Q and P, Set 9 (Hydrolysis) Review Exercises II, III (Anions)
11	Anions IV, V Cont. Sample 9 or practice sample	Review of Anions Chapter VIII	Work in chemistry of anions
12	General anion Sample all groups “Catch up,” period	Electrochemical Theory Chapter VIII	Q and P, Set 10 (Calculation of Potentials, etc.)
13	Single salt samples Sample 9a, 9b, etc. Salt mixtures	Systematic Analysis Exam on anions Chapter IX Sample 10	Review
14	Cont. Cont. if necessary	Interferences in Analysis	Review
15	* Alloy sample * Cont. if necessary	General review, Correlations of Cations and Anions * Final review or final exam	
16	Clean up Check out	* Final exam	* Alloy may have to be omitted if semester instruction ends at 15 weeks.

APPARATUS LIST

Each student's locker should contain the following equipment. Upon being assigned a locker, carefully check over the contents, and report shortages and imperfect apparatus to the instructor.

Non-Returnable List

4 sheets of drop-reaction paper.	1 towel.
2 crucibles.	1 sponge.
6 medicine droppers.	1 box of matches.
1 platinum wire.	1 two-hole rubber stopper to fit 50-ml. Erlenmeyer flask.
1 length of glass tubing.	1 spatula.
1 slide holder.	1 box of labels No. 4007.
1 pair of tweezers.	
1 nichrome wire triangle.	

Returnable List

12 centrifuge tubes (3-ml.).	1 50-ml. Erlenmeyer flask.
2 small watch glasses.	1 ringstand.
2 reagent blocks.	1 10-ml. graduate.
6 microscopic slides.	1 ring.
1 cobalt glass.	12 30-ml. bottles with droppers.
1 white spot plate.	48 screw-cap vials with dropping tubes (8-ml.).
1 burner (semi-micro or Bunsen).	
2 300-ml. beakers.	12 biological vials with corks.
1 100-ml. beaker.	

SOLID REAGENTS

Ammonium acetate, $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$	Lead acetate, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$
Ammonium chloride, NH_4Cl	Potassium chlorate, KClO_3
Ammonium iodide, NH_4I	Sodium acetate, $\text{NaC}_2\text{H}_3\text{O}_2$
Ammonium nitrate, NH_4NO_3	Sodium bismuthate, NaBiO_3
Ammonium persulfate, $(\text{NH}_4)_2\text{S}_2\text{O}_8$	Sodium carbonate, Na_2CO_3
Ammonium thiocyanate, NH_4SCN	Sodium peroxide, Na_2O_2
Borax, $\text{Na}_2\text{B}_4\text{O}_7$	Sodium nitrite, NaNO_2
Cobalt nitrate, $\text{Co}(\text{NO}_3)_2$	Sodium sulfite, Na_2SO_3
Ferrous sulfate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	

TEST PAPERS

Lead acetate.	Starch potassium iodide.
Litmus (neutral).	Turmeric.
Methyl orange.	

METALLIC REAGENTS

Aluminum foil.	Magnesium powder.	Zinc, arsenic-free.
Iron brads.	Platinum sheet.	Zinc, mossy or granular

LIQUID REAGENTS

Acetic Acid, $\text{HC}_2\text{H}_3\text{O}_2$, dilute. Dilute 12.5 ml. of glacial acetic acid to 100 ml. with water.

Alcohol, Amyl, $\text{C}_5\text{H}_{11}\text{OH}$. (Optional test reagent for acetates.)

Alcohol, Ethyl, $\text{C}_2\text{H}_5\text{OH}$. (Test reagent for acetates.)

Alcohol, Methyl, CH_3OH . (Test reagent for borates.)

Alizarin-S. Dissolve 0.1 gram in 100 ml. of water. (Test reagent for fluorides.)

Aluminon, $\text{C}_{19}\text{H}_9\text{O}_2$ (COONH_4)₃ (the ammonium salt of aurin-tricarboxylic acid). Dissolve 0.1 gram of the dye in 100 ml. of water. (Test reagent for aluminum.)

Ammoniacal Silver Nitrate (Miller's Reagent). Dissolve 0.17 gram of AgNO_3 , 2.53 grams of KNO_3 , and 1.7 ml. of concentrated NH_4OH in water, and dilute to 100 ml. with water.

Ammonium Acetate, $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$. Dissolve 25 grams in 100 ml. of water.

Ammonium Carbonate, $(\text{NH}_4)_2\text{CO}_3$. Dissolve 10 grams in a mixture of 10 ml. of concentrated NH_4OH and 50 ml. of water, and then dilute with water to 100 ml.

Ammonium Chloride, NH_4Cl . Dissolve 20 grams of NH_4Cl in 100 ml. of water.

Ammonium Hydroxide, NH_4OH , concentrated. Sp. gr. 0.9.

Ammonium Hydroxide, dilute. Dilute 15 ml. of the concentrated reagent with 15 ml. of water.

Ammonium Molybdate, $(\text{NH}_4)_2\text{MoO}_4$. Dissolve 15 grams of $(\text{NH}_4)_2\text{MoO}_4$ in 300 ml. of water, and pour into 100 ml. of HNO_3 (sp. gr. 1.2). (Test reagent for phosphates.)

Ammonium Oxalate, $(\text{NH}_4)_2\text{C}_2\text{O}_4$. Dissolve 3.5 grams of $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ in 100 ml. of water. (Test reagent for calcium.)

Ammonium Polysulfide. To be purchased as such.

Ammonium Sulfate, $(\text{NH}_4)_2\text{SO}_4$. Dissolve 13 grams in 100 ml. of water. (Test reagent for strontium.)

Barium Acetate, $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$. Dissolve 13.7 grams in 100 ml. of water.

Barium Chloride, BaCl_2 . Dissolve 25 grams of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ in 100 ml. of water. (Test reagent for sulfates.)

Barium Hydroxide, $\text{Ba}(\text{OH})_2$. Saturated solution. (Test reagent for carbonates.)

Barium Nitrate, $\text{Ba}(\text{NO}_3)_2$. Dissolve 6.5 grams in 100 ml. of water. (Anion group II reagent.)

α -Benzoinoxime, $\text{C}_6\text{H}_5\text{CHOH} \cdot \text{CNOH} \cdot \text{C}_6\text{H}_5$. Dissolve 5 grams in 100 ml. of 95 per cent alcohol. (Test reagent for copper.)

Bromine Water, Br_2 . Saturated solution.

Calcium Hydroxide, $\text{Ca}(\text{OH})_2$. Saturated solution of CaO in water.

Calcium Nitrate, $\text{Ca}(\text{NO}_3)_2$. Dissolve 23.6 grams of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in 100 ml. of water.

Calcium Sulfate, CaSO_4 . Saturated solution.

Chloroform, CHCl_3 .

Chloroplatinic Acid, H_2PtCl_6 . To be dispensed by the instructor. (Test reagent for potassium.)

Cinchonine Potassium Iodide. Dissolve 1 gram of cinchonine in 100 ml. of water, add a few drops of concentrated HNO_3 (sp. gr. 1.42), and warm until solution takes place. After cooling add 2 grams of KI. (Test reagent for bismuth.)

Cobalt Nitrate, $\text{Co}(\text{NO}_3)_2$. Saturated solution.

Dimethylamino Benzylidine Rhodanine. Dissolve 0.03 gram in 100 ml. of acetone. (Test reagent for silver.)

Dimethylglyoxime, $\text{C}_4\text{H}_8\text{N}_2\text{O}_2$. Dissolve 1 gram in 100 ml. of 95 per cent alcohol. (Test reagent for nickel.)

Diphenyl Carbazide, $[\text{C}_6\text{H}_5\text{NHNH}]_2\text{CO}$. Make a cold saturated solution of the reagent in 90 per cent alcohol, saturate with KCNS, and add a few crystals of KI. (Test reagent for mercury.)

Disodium Hydrogen Phosphate, Na_2HPO_4 . Dissolve 20 grams of the reagent in 100 ml. of water. (Test reagent for arsenates and phosphates.)

Ether, Ethyl ($\text{C}_2\text{H}_5)_2\text{O}$.

Ferric Chloride, FeCl_3 . Dissolve 10 grams of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in 100 ml. of water, and add 1 ml. of concentrated HNO_3 (sp. gr. 1.42).

Hydrochloric Acid, HCl , concentrated. Sp. gr. 1.19.

Hydrochloric Acid, HCl , dilute. Dilute 10 ml. of the concentrated reagent to 30 ml. with water (prepared by student).

Hydrogen Peroxide, H_2O_2 . The commercial 3 per cent solution.

Iodine, I_2 . Dissolve 0.127 gram in 100 ml. of water.

Magnesia Mixture. 10 grams of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, 10 grams of NH_4Cl and 5 ml. of conc. NH_3 solution dissolved and diluted to 100 ml. with water. (Test reagent for arsenates and phosphates.)

Mercuric Chloride, HgCl_2 . Saturated solution.

Nitric Acid, HNO_3 , concentrated. Sp. gr. 1.42.

Nitric Acid, HNO_3 , dilute. Dilute 10 ml. of the concentrated reagent to 30 ml. with water (prepared by student).

β -Nitrobenzene-Azoresorcinol, $\text{C}_{12}\text{H}_9\text{N}_3\text{O}_4$. Dissolve 0.001 gram of the substance in 100 ml. of 2 M NaOH. (Test reagent for magnesium.)

α -Nitroso- β -Naphthol, $\text{C}_{10}\text{H}_6\text{OH}(\text{NO})$. Make a saturated solution of the reagent in 50 per cent acetic acid. (Test reagent for cobalt.)

Orange IV. Dissolve 0.1 gram of Troponin OO in 100 ml. of water. (Test reagent for zinc.)

Perchloric Acid, HClO_4 . A 60 per cent solution. (Test reagent for potassium. Dispensed by instructor.)

Potassium Chromate, K_2CrO_4 . Dissolve 10 grams in 100 ml. of water. (Test reagent for lead and barium.)

Potassium Cyanide, KCN . Dissolve 5 grams in 100 ml. of water.

Potassium Ferricyanide, $\text{K}_3\text{Fe}(\text{CN})_6$. Dissolve 10 grams in 100 ml. of water.

Potassium Ferrocyanide, $\text{K}_4\text{Fe}(\text{CN})_6$. Dissolve 10 grams in 100 ml. of water.

Potassium Hydroxide, KOH . 4M. Dissolve 22.4 grams in 100 ml. of water (Division reagent for cation group II.)

Potassium Permanganate, KMnO_4 . Dissolve 1.5 grams in 100 ml. of water.

Resorcinol, $\text{C}_6\text{H}_6\text{O}_2$. Dissolve 1 gram in 50 ml. of concentrated H_2SO_4 (Test reagent for oxalates and tartrates.)

Rhodamine B. Dissolve 0.01 gram in 100 ml. of water. (Test reagent for antimony.)

Silver Acetate, $\text{AgC}_2\text{H}_3\text{O}_2$. Saturated solution.

Silver Nitrate, AgNO_3 . Dissolve 5 grams in 100 ml. of water.

Silver Nitrate, AgNO_3 . Dissolve 5 grams in 5 ml. of water. (To be dispensed by instructor. Test reagent for arsenic.)

Sodium Cobaltic Nitrite, $\text{Na}_3\text{Co}(\text{NO}_2)_6$. Dissolve 100 grams of NaNO_2 in 300 ml. of water, and add 10 ml. of glacial acetic acid and 10 grams of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. Allow to stand a day, and filter if necessary. Fresh reagent must be prepared frequently, since it is somewhat unstable. (Dispensed by instructor. Test reagent for potassium.)

Sodium Hydroxide, NaOH . Dissolve 120 grams, and make up to 100 ml. with water.

Sodium Hypochlorite, NaOCl . Commercial Zonite will serve the purpose.

Sodium Nitroprusside, $\text{Na}_2\text{Fe}(\text{CN})_5\text{NO}$. Dissolve 1 gram in 100 ml. of water. (Test reagent for sulfites.)

Stannous Chloride, SnCl_2 . Dissolve 20 grams of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in 100 ml. of dilute HCl. Add a small amount of granular tin.

Starch. Add 1 gram to 100 ml. of boiling water.

Sulfuric Acid, H_2SO_4 , concentrated. Sp. gr. 1.84.

Sulfuric Acid, H_2SO_4 , dilute. Pour 25 ml. of the concentrated reagent, slowly and with constant stirring, into 25 ml. of water (prepared by student).

Tartaric Acid, $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$. Saturated solution. (Test reagent for potassium.)

Zinc Nitrate, $\text{Zn}(\text{NO}_3)_2$. Dissolve 14.9 grams of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and make up to 100 ml. (Anion group III reagent.)

Zinc Sulfate, ZnSO_4 . Saturated solution of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$.

Zinc-Uranyl-Acetate. Dissolve 10 grams of uranyl acetate in 6 grams of 30 per cent acetic acid, warming, if necessary, and dilute to 50 ml. In a separate vessel mix 30 grams of zinc acetate with 3 grams of 30 per cent acetic acid, and dilute to 50 ml. Mix these two solutions, add a pinch of NaCl, allow to stand 24 hours, and then filter. (Test reagent for sodium.)

Zirconium Nitrate, $\text{Zr}(\text{NO}_3)_4$. Dissolve 0.1 gram in 20 ml. of conc. HCl, and dilute to 100 ml. with water. (Test reagent for fluorides.)

TEST SOLUTIONS OF CATIONS

Make stock test solutions by dissolving the weight given in the last column in water (or acids when indicated), and dilute to one liter. The stock solutions are of such strength that each milliliter contains 10 milligrams of the metallic ion. For student use, dilute the stock solution with 9 times its volume of water.

Cation	Salt	Grams per Liter
Ag^+	AgNO_3	15.7
Hg_2^{++}	$\text{Hg}_2(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ (a)	14.0
Pb^{++}	$\text{Pb}(\text{NO}_3)_2$	16.0
Hg^{++}	$\text{Hg}(\text{NO}_3)_2$ (a)	16.0
Bi^{+++}	$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (a)	23.0
Cu^{++}	$\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	46.5
Cd^{++}	$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	27.5
$\text{As}(-\text{ous})$	As_2O_3 (b)	13.2
$\text{As}(-\text{ic})$	As_2O_5	15.3
$\text{Sb}(-\text{ous})$	SbCl_3 (b)	19.0
Sn^{++}	$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (b)	19.0
$\text{Sn}(-\text{ic})$	SnCl_4	21.8
Ni^{++}	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	50.0
Co^{++}	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	50.0
Mn^{++}	$\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	53.0
Fe^{+++}	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	71.5
Al^{+++}	$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	70.0
Cr^{+++}	$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	77.0
Zn^{++}	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	45.5
Ba^{++}	$\text{Ba}(\text{NO}_3)_2$	19.0
Sr^{++}	$\text{Sr}(\text{NO}_3)_2$	24.0
Ca^{++}	$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	59.0
Mg^{++}	$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	16.0
K^+	KNO_3	26.0
Na^+	NaNO_3	37.0
NH_4^+	NH_4NO_3	44.5

(a) Use dilute HNO_3 to dissolve the salts.

(b) Use dilute HCl to dissolve the salts.

TEST SOLUTIONS OF ANIONS

Dissolve the indicated weight of salt in distilled water, and make up to one liter. This will give stock test solutions of such strength that each milliliter contains 50 milligrams of the non-metallic ion, with the exception of the oxalate (*) which directly contains 10 milligrams per milliliter. For student test solutions and for making unknowns, dilute the stock solution (except oxalate) with four times its volume of water.

Anion	Salt	Grams per Liter
CN ⁻	NaCN	95
NO ₂ ⁻	NaNO ₂	75
S ⁼	Na ₂ S·9H ₂ O	375
SO ₃ ⁻	Na ₂ SO ₃	80
S ₂ O ₃ ⁼	Na ₂ S ₂ O ₃ ·5H ₂ O	111
CO ₃ ⁼	Na ₂ CO ₃	88
AsO ₃ ⁼⁼	Na ₂ HAsO ₃	69
AsO ₄ ⁼⁼	Na ₂ HAsO ₄ ·12H ₂ O	152
PO ₄ ⁼⁼	Na ₂ HPO ₄ ·12H ₂ O	190
CrO ₄ ⁼⁼	K ₂ CrO ₄	85
SO ₄ ⁼⁼	Na ₂ SO ₄	75
BO ₃ ⁼⁼	Na ₂ B ₄ O ₇ ·10H ₂ O	81
SiO ₃ ⁻	Na ₂ SiO ₃	80
F ⁻	KF	152
C ₂ O ₄ ⁼⁼	Na ₂ C ₂ O ₄	15.2 *
C ₄ H ₄ O ₆ ⁼⁼	Na ₂ C ₄ H ₄ O ₆ ·2H ₂ O	78
Fe(CN) ₆ ⁼⁼	Na ₃ Fe(CN) ₆ ·H ₂ O	70.5
Fe(CN) ₆ ⁼⁼⁼⁼	Na ₄ Fe(CN) ₆ ·12H ₂ O	122.6
SCN ⁻	KCNS	87
I ⁻	KI	65
Br ⁻	KBr	75
Cl ⁻	NaCl	82.5
NO ₃ ⁻	NaNO ₃	68.5
C ₂ H ₃ O ₂ ⁻	NaC ₂ H ₃ O ₂ ·3H ₂ O	115
ClO ₃ ⁻	KClO ₃	73.4

TABLE XXVIII
SOLUBILITY-PRODUCT CONSTANTS

A. Halides

AgCl	1.1×10^{-10}	PbCl ₂	1.7×10^{-5}	Hg ₂ Cl ₂	2.0×10^{-18}
AgBr	3.5×10^{-13}	PbBr ₂	7.4×10^{-5}	Hg ₂ Br ₂	5.2×10^{-23}
AgI	1.6×10^{-16}	PbI ₂	8.7×10^{-9}	Hg ₂ I ₂	1.1×10^{-28}

B. Alkaline Earth Salts

<i>Carbonates</i>	<i>Sulfates</i>	<i>Chromates</i>
CaCO ₃	1.7×10^{-8}	CaCrO ₄
	9.3×10^{-8}	SrCrO ₄
SrCO ₃	1.6×10^{-9}	BaCrO ₄
BaCO ₃	8.1×10^{-9}	
MgCO ₃	1×10^{-5}	

C. Sulfides

HgS	4.1×10^{-53}	Bi ₂ S ₃	
Ag ₂ S	1×10^{-49}	SnS	1×10^{-29}
Hg ₂ S	1×10^{-45}	CdS	3.6×10^{-29}
CuS	8.5×10^{-45}	PbS	4.0×10^{-28}
As ₂ S ₃		ZnS	1.2×10^{-23}
As ₂ S ₅		CoS	1×10^{-22}
Sb ₂ S ₃	1×10^{-30}	NiS	1×10^{-21}
Sb ₂ S ₅		FeS	1×10^{-19}
		MnS	1×10^{-15}

D. Miscellaneous

CaCrO ₄	2.6×10^{-9}	Fe(OH) ₃	1.1×10^{-36}
PbSO ₄	1.8×10^{-8}	Fe(OH) ₂	1.6×10^{-14}
PbCrO ₄	1.7×10^{-14}	K ₂ PtCl ₆	4.9×10^{-5}
MgCO ₃	1×10^{-5}	BiOCl	7×10^{-9}
MgNH ₄ PO ₄	2.5×10^{-13}	CaF ₂	3.9×10^{-11}
Mg(OH) ₂	3.5×10^{-11}		

TABLE XXIX
INSTABILITY CONSTANTS

A. Complex Ammines

$\text{Ag}(\text{NH}_3)_2^+$	6.8×10^{-8}	$\text{Zn}(\text{NH}_3)_4^{++}$	2.6×10^{-10}
$\text{Cu}(\text{NH}_3)_4^{++}$	4.6×10^{-14}	$\text{Ni}(\text{NH}_3)_4^{++}$	4.8×10^{-8}
$\text{Cd}(\text{NH}_3)_4^{++}$	1×10^{-7}	$\text{Co}(\text{NH}_3)_4^{++}$	1.3×10^{-5}

$\text{Co}(\text{NH}_3)_6^{+++}$ 2.2×10^{-34}

B. Complex Cyanides

$\text{Ag}(\text{CN})_2^-$	4×10^{-19}	$\text{Hg}(\text{CN})_4^{=}$	4×10^{-42}
$\text{Ag}(\text{CN})_3^{=}$	8×10^{-23}	$\text{Fe}(\text{CN})_6^{=}$	1×10^{-44}
$\text{Cu}(\text{CN})_3^{=}$	5×10^{-28}	$\text{Fe}(\text{CN})_6^{==}$	1×10^{-37}
$\text{Cd}(\text{CN})_4^{==}$	1.4×10^{-17}	$\text{Au}(\text{CN})_2^{--}$	5×10^{-39}
$\text{Ni}(\text{CN})_4^{==}$	1×10^{-22}		
$\text{Zn}(\text{CN})_4^{==}$	2×10^{-17}		

C. Complex Halide and Other Complex Ions

$\text{HgCl}_4^{=}$	1×10^{-16}	$\text{CdI}_4^{=}$	5×10^{-7}
$\text{HgBr}_4^{=}$	2×10^{-22}	AuCl_4^-	5×10^{-22}
$\text{HgI}_4^{=}$	5×10^{-31}		

Other Complex Ions

$\text{Fe}(\text{SCN})_6^{=}$	8×10^{-10}	$\text{Ag}(\text{S}_2\text{O}_3)_2^{=}$	1×10^{-21}
$\text{Hg}(\text{SCN})_4^{=}$	1×10^{-22}		

TABLE XXX

IONIZATION CONSTANTS

<i>Electrolyte</i>	<i>Primary</i>	<i>Secondary</i>	<i>Tertiary</i>
HCl	*		
HNO ₃	*		
HNO ₂	5×10^{-4}		
HCHO ₂	2×10^{-4}		
HC ₂ H ₃ O ₂	1.8×10^{-5}		
HCN	7×10^{-10}		
H ₂ SO ₄	*	1.2×10^{-2}	
H ₂ C ₂ O ₄	6.5×10^{-2}	6×10^{-5}	
H ₂ C ₄ H ₄ O ₆	9.7×10^{-4}	3×10^{-5}	
H ₂ SO ₃	1.7×10^{-2}	1×10^{-7}	
H ₂ CO ₃	3×10^{-7}	5×10^{-11}	
H ₂ S†	6×10^{-8}	1.2×10^{-15}	
H ₃ AsO ₄	5×10^{-3}	4×10^{-5}	6×10^{-10}
H ₃ PO ₄	1×10^{-2}	7×10^{-8}	4×10^{-13}
HAsO ₂	6×10^{-10}		
H ₃ PO ₃	6×10^{-10}		
HOH‡	2×10^{-16}		
NaOH	*		
NH ₄ OH	1.75×10^{-5}		
Ca(OH) ₂	3×10^{-2}		

* Ionization too great to yield an ionization constant.

$$\dagger \frac{(C_{\text{H}^+})^2 \times C_{\text{S}^-}}{C_{\text{H}_2\text{S}}} = 1.1 \times 10^{-22}; (C_{\text{H}^+})^2 \times C_{\text{S}^-} = 1.1 \times 10^{-23}.$$

$$\ddagger C_{\text{H}^+} \times C_{\text{OH}^-} = 1.2 \times 10^{-14}.$$

DENSITY OF AMMONIA SOLUTIONS AT 15° C.

(According to Lunge and Wiernik)

Specific Gravity	Per Cent NH ₃	Specific Gravity	Per Cent NH ₃
1.000	0.00	0.940	15.63
0.998	0.45	0.938	16.22
0.996	0.91	0.936	16.82
0.994	1.37	0.934	17.42
0.992	1.84	0.932	18.03
0.990	2.31	0.930	18.64
0.988	2.80	0.928	19.25
0.986	3.30	0.926	19.87
0.984	3.80	0.924	20.49
0.982	4.30	0.922	21.12
0.980	4.80	0.920	21.75
0.978	5.30	0.918	22.39
0.976	5.80	0.916	23.03
0.974	6.30	0.914	23.68
0.972	6.80	0.912	24.33
0.970	7.31	0.910	24.99
0.968	7.82	0.908	25.65
0.966	8.33	0.906	26.31
0.964	8.84	0.904	26.98
0.962	9.35	0.902	27.65
0.960	9.91	0.900	28.33
0.958	10.47	0.898	29.01
0.956	11.03	0.896	29.69
0.954	11.60	0.894	30.37
0.952	12.17	0.892	31.05
0.950	12.74	0.890	31.75
0.948	13.31	0.888	32.50
0.946	13.88	0.886	33.25
0.944	14.46	0.884	34.10
0.942	15.04	0.882	34.95

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APPENDIX B

DENSITY OF STRONG ACIDS AT 15° C. IN VACUO
 (According to Lunge, Isler, Naef, and Marchlewsky)

Specific Gravity at $\frac{15^{\circ}}{4^{\circ}}$ (Vacuo)	Per Cent by Weight			Specific Gravity at $\frac{15^{\circ}}{4^{\circ}}$ (Vacuo)	Per Cent by Weight	
	HCl	HNO ₃	H ₂ SO ₄		HNO ₃	H ₂ SO ₄
1.000	0.16	0.10	0.09	1.235	37.51	31.70
1.005	1.15	1.00	0.95	1.240	38.27	32.28
1.010	2.14	1.90	1.57	1.245	39.03	32.86
1.015	3.12	2.80	2.30	1.250	39.80	33.43
1.020	4.13	3.70	3.03	1.255	40.56	34.00
1.025	5.15	4.60	3.76	1.260	41.32	34.57
1.030	6.15	5.50	4.49	1.265	42.08	35.14
1.035	7.15	6.38	5.23	1.270	42.85	35.71
1.040	8.16	7.26	5.96	1.275	43.62	36.29
1.045	9.16	8.13	6.67	1.280	44.39	36.87
1.050	10.17	8.99	7.37	1.285	45.16	37.45
1.055	11.18	9.84	8.07	1.290	45.93	38.03
1.060	12.19	10.67	8.77	1.295	46.70	38.61
1.065	13.19	11.50	9.47	1.300	47.47	39.19
1.070	14.17	12.32	10.19	1.305	48.24	39.77
1.075	15.16	13.14	10.90	1.310	49.05	40.35
1.080	16.15	13.94	11.60	1.315	49.88	40.93
1.085	17.13	14.73	12.30	1.320	50.69	41.50
1.090	18.11	15.52	12.99	1.325	51.51	42.08
1.095	19.06	16.31	13.67	1.330	52.34	42.66
1.100	20.01	17.10	14.35	1.335	53.17	43.20
1.105	20.97	17.88	15.03	1.340	54.04	43.74
1.110	21.92	18.66	15.71	1.345	54.90	44.28
1.115	22.86	19.44	16.36	1.350	55.76	44.82
1.120	23.82	20.22	17.01	1.355	56.63	45.35
1.125	24.78	20.99	17.66	1.360	57.54	45.88
1.130	25.75	21.76	18.31	1.365	58.45	46.41
1.135	26.70	22.53	18.96	1.370	59.36	46.94
1.140	27.66	23.30	19.61	1.375	60.27	47.47
1.145	28.61	24.07	20.26	1.380	61.24	48.00
1.150	29.57	24.83	20.91	1.385	62.21	48.53
1.155	30.55	25.59	21.55	1.390	63.20	49.06
1.160	31.52	26.35	22.19	1.395	64.22	49.59
1.165	32.49	27.11	22.83	1.400	65.27	50.11
1.170	33.46	27.87	23.47	1.405	66.37	50.63
1.175	34.42	28.62	24.12	1.410	67.47	51.15
1.180	35.39	29.37	24.76	1.415	68.60	51.66
1.185	36.31	30.12	25.40	1.420	69.77	52.15
1.190	37.23	30.87	26.04	1.425	70.95	52.63
1.195	38.16	31.60	26.68	1.430	72.14	53.11
1.200	39.11	32.34	27.32	1.435	73.35	53.59
1.205	33.07	27.95	1.440	74.64	54.07
1.210	33.80	28.58	1.445	75.94	54.55
1.215	34.53	29.21	1.450	77.24	55.03
1.220	35.26	29.84	1.455	78.56	55.50
1.225	36.01	30.48	1.460	79.94	55.97
1.230	36.76	31.11	1.465	81.38	56.43

Specific Gravity at $\frac{15^{\circ}}{4^{\circ}}$ (Vacuo)	Per Cent by Weight HNO ₃	Per Cent by Weight H ₂ SO ₄	Specific Gravity at $\frac{15^{\circ}}{4^{\circ}}$ (Vacuo)	Per Cent by Weight H ₂ SO ₄	Specific Gravity at $\frac{15^{\circ}}{4^{\circ}}$ (Vacuo)	Per Cent by Weight H ₂ SO ₄
1.470	82.86	56.90	1.610	69.56	1.750	81.56
1.475	84.41	57.37	1.615	70.00	1.755	82.00
1.480	86.01	57.83	1.620	70.42	1.760	82.44
1.485	87.66	58.28	1.625	70.85	1.765	83.01
1.490	89.86	58.74	1.630	71.27	1.770	83.51
1.495	91.56	59.22	1.635	71.70	1.775	84.02
1.500	94.04	59.70	1.640	72.12	1.780	84.50
1.505	96.34	60.18	1.645	72.55	1.785	85.10
1.510	98.05	60.65	1.650	72.96	1.790	85.70
1.515	99.02	61.12	1.655	73.40	1.795	86.30
1.520	99.62	61.59	1.660	73.81	1.800	86.92
1.525	62.06	1.665	74.24	1.805	87.60
1.530	62.53	1.670	74.66	1.810	88.30
1.535	63.00	1.675	75.08	1.815	89.16
1.540	63.43	1.680	75.50	1.820	90.05
1.545	63.85	1.685	75.94	1.825	91.00
1.550	64.26	1.690	76.38	1.830	92.10
1.555	64.67	1.695	76.76	1.835	93.56
1.560	65.20	1.700	77.17	1.840	95.60
1.565	65.65	1.705	77.60	1.8405	95.95
1.570	66.09	1.710	78.04	1.8410	96.38
1.575	66.53	1.715	78.48	1.8415	97.35
1.580	66.95	1.720	78.92	1.8410	98.20
1.585	67.40	1.725	79.36	1.8405	98.52
1.590	67.83	1.730	79.80	1.8400	98.72
1.595	68.26	1.735	80.24	1.8395	98.77
1.600	68.70	1.740	80.68	1.8390	99.12
1.605	69.13	1.745	81.12	1.8385	99.31

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SOLUBILITY TABLE

	Ag^{+}	Pb^{++} (1)	Hg^{++} (1)	Bi^{++} (2)	Cu^{++}	Cd^{++}	As^{++}	Sb^{++} (2)	Sn^{++}	Ni^{++}	Co^{++}	Fe^{++}
Nitrite, NO_2^-	Hof W	W	W	—	W	W	—	—	W	W	W	—
Sulfide, S^-	HNO_3	HNO_3	HNO_3	ac. reg.	HNO_3	HNO_3	HNO_3	HNO_3	—	—	strong HCl	HNO_3
Sulfite, SO_3^{2-}	HNO_3	HNO_3	HNO_3	—	HCl	HCl	—	—	HCl	HCl	HCl	HCl
Thiosulfate, $\text{S}_2\text{O}_3^{2-}$	HNO_3	HNO_3	HNO_3	—	—	W	—	—	W	W	W	W
Carbonate, CO_3^{2-}	HNO_3	HNO_3	HNO_3	—	HCl	HCl	HCl	HCl	—	—	HCl	HCl
Arsenite, AsO_3^{3-}	HNO_3	HNO_3	HNO_3	—	HCl	HCl	HCl	HCl	—	—	HCl	HCl
Arsenate, AsO_4^{3-}	HNO_3	HNO_3	HNO_3	—	HCl	HCl	HCl	HCl	—	—	HCl	HCl
Phosphate, PO_4^{3-}	HNO_3	HNO_3	HNO_3	—	HCl	HCl	HCl	HCl	—	—	HCl	HCl
Chromate, CrO_4^{2-}	HNO_3	HNO_3	HNO_3	—	HCl	HCl	HCl	HCl	—	—	HCl	—
Sulfate, SO_4^{2-}	Sl. W	Sl. W	Sl. W	Ins.	Sl. W	W	W	W	—	W	W	W
Borate, BO_3^{2-}	HNO_3	HNO_3	HNO_3	—	—	HCl	HCl	HCl	—	HCl	HCl	HCl
Silicate, SiO_3^{2-}	(3)	HNO_3	HNO_3	—	—	HCl	HCl	HCl	—	HCl	HCl	HCl
Fluoride, F^-	W	Sl. W	W	—	HCl	HCl	HCl	HCl	Sl. W	W	HCl	Sl. W
Oralate, $\text{C}_2\text{O}_4^{2-}$	(4)	HNO_3	HNO_3	—	HCl	HCl	HCl	HCl	HCl	HCl	HCl	HCl
Tartrate, $\text{C}_4\text{H}_4\text{O}_6$	(4)	HNO_3	HNO_3	—	HCl	HCl	HCl	HCl	HCl	HCl	HCl	HCl
Ferricyanide, $\text{Fe}(\text{CN})_6^{4-}$	Ins.	Ins.	Ins.	—	Ins.	Ins.	Ins.	Ins.	—	Ins.	Ins.	Ins.
Ferrocyanide, $\text{Fe}(\text{CN})_6^{4-}$	Ins.	Ins.	Ins.	—	Ins.	Ins.	Ins.	Ins.	—	Ins.	Ins.	Ins.
Thiocyanate, CNS^-	Ins.	HNO_3	HNO_3	—	HNO_3	HCl	HCl	HCl	—	W	W	W
Cyanide, CN^-	Ins.	HNO_3	W	—	—	—	—	—	—	—	HNO_3	Ins.
Iodide, I^-	Ins.	HNO_3	HNO_3	—	HCl	HCl	HCl	HCl	Sl. W	W	Hyd. W	W
Bromide, Br^-	Ins.	Ins.	HNO_3	W	Hyd. W	W	W	W	Hyd. W	W	W	W
Chloride, Cl^-	Ins.	Hot W	HNO_3	W	Hyd. W	W	W	W	Hyd. W	W	W	W
Acetate, $\text{C}_2\text{H}_3\text{O}_2^-$	Sl. W	W	W	W	W	W	W	W	W	W	W	W
Nitrate, NO_3^-	W	W	Sl. W	HNO_3	W	W	W	W	—	W	W	W
Oxide, $(\text{O} =)$	—	HNO_3	HNO_3	—	HCl	HNO_3	HCl	HCl	—	HCl	HCl	HCl
Hydroxide, OH^-	—	HNO_3	HNO_3	—	—	HCl	HCl	HCl	—	HCl	HCl	HCl

W = water-soluble (solubility at least 1 gram of the salt in 100 cc. of water); Aq. reg. = soluble in aqua regia;

Sl. W = slightly soluble in water (solubility about 0.1 gram per 100 cc. of water); Ins. = insoluble in acids taken singly or together;

Hyd. W = hydrolyzed by water, yielding a product not soluble in water;

HCl = soluble in hydrochloric acid;

HNO_3 = soluble in nitric acid;

— = compound either does not exist or the proper solvent has not been determined.

SOLUBILITY TABLE (Continued)

	Fe+++	Mn++	Al+++	Cr+++	Zn++	Ba++	Sr++	Ca++	Mg++	NH4+	K+	Na+	Free Acid (H+)
Nitrite, NO_3^-	W	W	—	Hyd. W	W	W	W	W	W	W	W	W	(gas)
Sulfide, S^{2-}	HCl	HCl	HCl	HCl	W	W	W	W	W	W	W	W	(gas)
Sulfite, SO_3^{2-}	—	HCl	HCl	—	HCl	HCl	HCl	W	W	W	W	W	(gas)
Thiosulfate, $\text{S}_2\text{O}_3^{2-}$	—	W	W	—	W	HCl	W	W	W	W	W	W	—
Carbonate, CO_3^{2-}	—	HCl	—	—	HCl	HCl	HCl	W	W	W	W	W	(gas)
Arsenite, AsO_3^{3-}	HCl	HCl	—	—	HCl	HCl	HCl	HCl	HCl	W	W	W	—
Arsenate, AsO_4^{3-}	HCl	HCl	HCl	HCl	HCl	HCl	HCl	HCl	HCl	W	W	W	(solid)
Phosphate, PO_4^{3-}	HCl	HCl	HCl	HCl	HCl	HCl	HCl	HCl	HCl	W	W	W	(liquid)
Chromate, CrO_4^{2-}	W	Sl. W	HCl	—	HCl	W	W	W	W	W	W	W	(solid)
Sulfate, SO_4^{2-}	W	W	W	W	W	Ins.	Ins.	Sl. W	W	W	W	W	(liquid)
Borate, BO_3^{3-}	HCl	HCl	HCl	HCl	HCl	HCl	HCl	Sl. W	HCl	W	W	W	(solid)
Silicate, SiO_4^{4-}(3)	HCl	HCl	HCl	HCl	HCl	HCl	HCl	HCl	HCl	W	W	W	(solid)
Fluoride, F^-	Sl. W	Sl. W	HCl	W	HCl	HCl	HCl	Sl. W	HCl	W	W	W	(gas)
Oxalate, $\text{C}_2\text{O}_4^{2-}$(4)	HCl	HCl	HCl	HCl	HCl	HCl	HCl	HCl	HCl	W	W	W	(solid)
Tartrate, $\text{C}_4\text{H}_4\text{O}_6$(4)	W	Sl. W	W	HCl	W	HCl	HCl	HCl	HCl	W	W	W	(solid)
Ferricyanide, $\text{Fe}(\text{CN})_6^{4-}$	W	Ins.	—	—	HCl	W	W	W	W	W	W	W	(solid)
Ferrocyanide, $\text{Fe}(\text{CN})_6^{4-}$	W	HCl	—	—	Ins.	W	W	W	W	W	W	W	(solid)
Thiocyanate, CNS^-	W	W	W	W	W	W	W	W	W	W	W	W	(gas)
Cyanide, CN^-	—	HCl	—	HCl	HCl	Sl. W	W	W	W	W	W	W	(gas)
Iodide, I^-	W	W	W	W	W	W	W	W	W	W	W	W	(gas)
Bromide, Br^-	W	W	W	W	W	W	W	W	W	W	W	W	(gas)
Chloride, Cl^-	W	W	W	W	W	W	W	W	W	W	W	W	(gas)
Acetate, $\text{C}_2\text{H}_3\text{O}_2^-$	W	W	W	W	W	W	W	W	W	W	W	W	(liquid)
Nitrate, NO_3^-	W	W	W	W	W	W	W	W	W	W	W	W	(liquid)
Oxide, (O^-)	HCl	HCl	HCl	HCl	HCl	HCl	HCl	HCl	HCl	—	W	W	—
Hydroxide, OH^-	HCl	HCl	HCl	HCl	HCl	HCl	HCl	W	Sl. W	Sl. W	HCl	W	(liquid)

(1) Addition of HCl will transpose many salts of silver, lead, and mercurous mercury into insoluble chlorides.
 (2) Many salts of bismuth and antimony show marked hydrolysis with precipitation of water-insoluble products.

(3) The solubility here refers to freshly precipitated and not to native silicates.
 (4) Many tartrates and oxalates are soluble in aqueous solutions containing excess tartrate or oxalate ions.

APPENDIX B

LOGARITHMS

Natural Numbers										PROPORTIONAL PARTS									
	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	8	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7

LOGARITHMS

Natural Numbers	PROPORTIONAL PARTS										1	2	3	4	5	6	7	8	9	
	0	1	2	3	4	5	6	7	8	9										
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	I	2	2	3	4	5	5	6	7	
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	I	2	2	3	4	5	5	6	7	
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	I	2	2	3	4	5	5	6	7	
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	I	1	2	3	4	5	5	6	7	
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	I	1	2	3	4	4	5	6	7	
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	I	I	2	3	4	4	5	6	6	
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	I	I	2	3	4	4	5	6	6	
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	I	I	2	3	4	5	5	6	6	
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	I	I	2	3	3	4	5	5	6	
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	I	I	2	3	3	4	5	5	6	
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	I	I	2	3	3	4	5	5	6	
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	I	I	2	3	3	4	5	5	6	
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	I	I	2	3	3	4	5	5	6	
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8383	I	I	2	3	3	4	4	5	6	
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	I	I	2	3	3	4	4	5	6	
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	I	I	2	2	3	4	4	5	6	
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	I	I	2	2	3	4	4	5	5	
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	I	I	2	2	3	4	4	5	5	
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	I	I	2	2	3	4	4	5	5	
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	I	I	2	2	3	4	4	5	5	
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	I	I	2	2	3	3	4	5	5	
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	I	I	2	2	3	3	4	5	5	
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	I	I	2	2	3	3	4	4	5	
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	I	I	2	2	3	3	4	4	5	
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9026	I	I	2	2	3	3	4	4	5	
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	I	I	2	2	3	3	4	4	5	
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	I	I	2	2	3	3	4	4	5	
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	I	I	2	2	3	3	4	4	5	
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	I	I	2	2	3	3	4	4	5	
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	I	I	2	2	3	3	4	4	5	
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	I	I	2	2	3	3	4	4	5	
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	I	I	2	2	3	3	4	4	5	
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	O	I	I	2	2	3	3	4	4	
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	O	I	I	2	2	3	3	4	4	
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	O	I	I	2	2	3	3	4	4	
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	O	I	I	2	2	3	3	4	4	
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	O	I	I	2	2	3	3	4	4	
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	O	I	I	2	2	3	3	4	4	
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	O	I	I	2	2	3	3	4	4	
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	O	I	I	2	2	3	3	4	4	
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	O	I	I	2	2	3	3	4	4	
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	O	I	I	2	2	3	3	4	4	
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	O	I	I	2	2	3	3	4	4	
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	O	I	I	2	2	3	3	4	4	
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	O	I	I	2	2	3	3	4	4	

APPENDIX B

ANTILOGARITHMS

Logarithms	0	1	2	3	4	5	6	7	8	9	PROPORTIONAL PARTS								
	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9	
.00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0	0	I	I	I	I	I	2	2
.01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0	0	I	I	I	I	I	2	2
.02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0	0	I	I	I	I	I	2	2
.03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0	0	I	I	I	I	I	2	2
.04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0	I	I	I	I	I	2	2	2
.05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0	I	I	I	I	I	2	2	2
.06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0	I	I	I	I	I	2	2	2
.07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0	I	I	I	I	I	2	2	2
.08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0	I	I	I	I	I	2	2	3
.09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0	I	I	I	I	I	2	2	3
.10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0	I	I	I	I	I	2	2	3
.11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0	I	I	I	I	I	2	2	3
.12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0	I	I	I	I	I	2	2	3
.13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0	I	I	I	I	I	2	2	3
.14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0	I	I	I	I	I	2	2	3
.15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0	I	I	I	I	I	2	2	3
.16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0	I	I	I	I	I	2	2	3
.17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0	I	I	I	I	I	2	2	3
.18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0	I	I	I	I	I	2	2	3
.19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0	I	I	I	I	I	2	2	3
.20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0	I	I	I	I	I	2	2	3
.21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0	I	I	I	I	I	2	2	3
.22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0	I	I	I	I	I	2	2	3
.23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0	I	I	I	I	I	2	2	3
.24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0	I	I	I	I	I	2	2	3
.25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0	I	I	I	I	I	2	2	3
.26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0	I	I	I	I	I	2	2	3
.27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0	I	I	I	I	I	2	2	3
.28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0	I	I	I	I	I	2	2	3
.29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0	I	I	I	I	I	2	2	3
.30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0	I	I	I	I	I	2	2	3
.31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0	I	I	I	I	I	2	2	3
.32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0	I	I	I	I	I	2	2	3
.33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0	I	I	I	I	I	2	2	3
.34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	I	I	I	I	I	2	2	3	4
.35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	I	I	I	I	I	2	2	3	4
.36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	I	I	I	I	I	2	2	3	4
.37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	I	I	I	I	I	2	2	3	4
.38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	I	I	I	I	I	2	2	3	4
.39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	I	I	I	I	I	2	2	3	4
.40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	I	I	I	I	I	2	2	3	4
.41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	I	I	I	I	I	2	2	3	4
.42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	I	I	I	I	I	2	2	3	4
.43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	I	I	I	I	I	2	2	3	4
.44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	I	I	I	I	I	2	2	3	4
.45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	I	I	I	I	I	2	2	3	4
.46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	I	I	I	I	I	2	2	3	4
.47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	I	I	I	I	I	2	2	3	4
.48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	I	I	I	I	I	2	2	3	4
.49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	I	I	I	I	I	2	2	3	4

ANTILOGARITHMS

Loga- rithms										PROPORTIONAL PARTS										
	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9	
.50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	I	I	2	3	4	4	4	5	6	7
.51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	I	2	2	3	4	5	5	6	7	
.52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	I	2	2	3	4	5	5	6	7	
.53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	I	2	2	3	4	5	6	6	7	
.54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	I	2	2	3	4	5	6	6	7	
.55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	I	2	2	3	4	5	6	7	7	
.56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	I	2	3	3	4	5	5	6	8	
.57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	I	2	3	3	4	5	6	7	8	
.58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	I	2	3	4	4	5	6	7	8	
.59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972	I	2	3	4	5	5	6	7	8	
.60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	I	2	3	4	5	6	6	7	8	
.61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	I	2	3	4	5	6	7	8	9	
.62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	I	2	3	4	5	6	7	8	9	
.63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	I	2	3	4	5	6	7	8	9	
.64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	I	2	3	4	5	6	7	8	9	
.65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	I	2	3	4	5	6	7	8	9	
.66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	I	2	3	4	5	6	7	9	10	
.67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	I	2	3	4	5	7	8	9	10	
.68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	I	2	3	4	6	7	8	9	10	
.69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	I	2	3	5	6	7	8	9	10	
.70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	I	2	4	5	6	7	8	9	11	
.71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	I	2	4	5	6	7	8	10	11	
.72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	I	2	4	5	6	7	9	10	11	
.73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	I	3	4	5	6	8	9	10	11	
.74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	I	3	4	5	6	8	9	10	12	
.75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	I	3	4	5	7	8	9	10	12	
.76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	I	3	4	5	7	8	9	11	12	
.77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	I	3	4	5	7	8	10	11	12	
.78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	I	3	4	6	7	8	10	11	13	
.79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	I	3	4	6	7	9	10	11	13	
.80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	I	3	4	6	7	9	10	12	13	
.81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	I	2	3	5	6	8	9	11	14	
.82	6607	6622	6637	6653	6668	6683	6709	6714	6730	6745	I	2	3	5	6	8	9	11	14	
.83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	I	2	3	5	6	8	9	11	14	
.84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	I	2	3	5	6	8	10	11	15	
.85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	I	2	3	5	7	8	10	12	15	
.86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	I	2	3	5	7	8	10	12	15	
.87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	I	2	3	5	7	9	10	12	14	
.88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	I	2	4	5	7	9	11	12	14	
.89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	I	2	4	5	7	9	11	13	14	
.90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	I	2	4	6	7	9	11	13	17	
.91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	I	2	4	6	8	9	11	13	17	
.92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	I	2	4	6	8	10	12	14	17	
.93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	I	2	4	6	8	10	12	14	18	
.94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	I	2	4	6	8	10	12	14	18	
.95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	I	2	4	6	8	10	12	15	19	
.96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	I	2	4	6	8	11	13	15	19	
.97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	I	2	4	7	9	11	13	15	20	
.98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	I	2	4	7	9	11	13	16	20	
.99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977	I	2	5	7	9	11	14	16	20	

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INTERNATIONAL ATOMIC WEIGHTS

1947

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	<i>Symbol</i>	<i>Atomic Number</i>	<i>Atomic Weight</i>		<i>Symbol</i>	<i>Atomic Number</i>	<i>Atomic Weight</i>
Aluminum....	Al	13	26.97	Molybdenum..	Mo	42	95.95
Antimony....	Sb	51	121.76	Neodymium..	Nd	60	144.27
Argon.....	A	18	39.944	Neon.....	Ne	10	20.183
Arsenic....	As	33	74.91	Nickel.....	Ni	28	58.69
Barium.....	Ba	56	137.36	Nitrogen.....	N	7	14.008
Beryllium....	Be	4	9.02	Osmium.....	Os	76	190.2
Bismuth....	Bi	83	209.00	Oxygen.....	O	8	16.0000
Boron.....	B	5	10.82	Palladium....	Pd	46	106.7
Bromine....	Br	35	79.916	Phosphorus...	P	15	30.98
Cadmium....	Cd	48	112.41	Platinum....	Pt	78	195.23
Calcium....	Ca	20	40.08	Potassium....	K	19	39.096
Carbon....	C	6	12.010	Praseodymium	Pr	59	140.92
Cerium....	Ce	58	140.13	Protactinium.	Pa	91	231
Cesium....	Cs	55	132.91	Radium.....	Ra	88	226.05
Chlorine....	Cl	17	35.457	Radon.....	Rn	86	222
Chromium....	Cr	24	52.01	Rhenium....	Re	75	186.31
Cobalt....	Co	27	58.94	Rhodium....	Rh	45	102.91
Columbium..	Cb	41	92.91	Rubidium....	Rb	37	85.48
Copper....	Cu	29	63.54	Ruthenium...	Ru	44	101.7
Dysprosium..	Dy	66	162.46	Samarium....	Sm	62	150.43
Erbium....	Er	68	167.2	Scandium....	Sc	21	45.10
Europium....	Eu	63	152.0	Selenium....	Se	34	78.96
Fluorine....	F	9	19.00	Silicon.....	Si	14	28.06
Gadolinium..	Cd	64	156.9	Silver.....	Ag	47	107.880
Gallium....	Ca	31	69.72	Sodium.....	Na	11	22.997
Germanium....	Ge	32	72.60	Strontium....	Sr	38	87.63
Gold.....	Au	79	197.2	Sulfur.....	S	16	32.066
Hafnium....	Hf	72	178.6	Tantalum....	Ta	73	180.88
Helium....	He	2	4.003	Tellurium....	Te	52	127.61
Holmium....	Ho	67	164.94	Terbium....	Tb	65	159.2
Hydrogen....	H	1	1.0080	Thallium....	Tl	81	204.39
Indium....	In	49	114.76	Thorium....	Th	90	232.12
Iodine....	I	53	126.92	Thulium....	Tm	69	169.4
Iridium....	Ir	77	193.1	Tin.....	Sn	50	118.70
Iron.....	Fe	26	55.85	Titanium....	Ti	22	47.90
Krypton....	Kr	36	83.7	Tungsten....	W	74	183.92
Lanthanum..	La	57	138.92	Uranium....	U	92	238.07
Lead.....	Pb	82	207.21	Vanadium....	V	23	50.95
Lithium....	Li	3	6.940	Xenon.....	Xe	54	131.3
Lutecium....	Lu	71	174.99	Ytterbium....	Yb	70	173.04
Magnesium..	Mg	12	24.32	Yttrium....	Y	39	88.92
Manganese...	Mn	25	54.93	Zinc.....	Zn	30	65.38
Mercury....	Hg	80	200.61	Zirconium....	Zr	40	91.22

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